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CHRONOPOTENTIOMETRY IN FUSED LITHIUM CHLORIDE-POTASSIUM CHLORIDE

by

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INTRODUCTION

The principles of chronopotentiometry have been known for a long time. In aqueous medium some of the early applications date as far back as 78 years. This technique was used by WEBER[1] (1879) and SAND[2] (1901) in calculating the concentration at the the electrode of a solution of a single salt from which the metal was being deposited under the condition that diffusion and migration were the sole modes of transport of the ions to the electrode. The equations derived by the solution of Fick's diffusion law under the above conditions were verified, and the diffusion coefficients of several salts were determined. Thirty years later this principle was applied by BUTLER AND ARMSTRONG[3,4] in the study of the kinetics of simple processes involving reduction of aniline blue and the cathodic and anodic behavior of quinhydrone at platinum electrode. However, the practical potentialities of this method were not revealed until the first comprehensive work was reported by GIERST AND JULIARD[5,6] (1953), who also devised an ingenious experimental arrangement for the oscillographic recording of the potential-time curves. The theory of electrolysis at constant current has been considered in detail by DELAHAY *et al.*[7-11], who have mathematically analyzed the various diffusion problems corresponding to specific electrode processes. DELAHAY AND MAMANTOV[12] have recently reviewed the theoretical principles and examined potentialities of this method as an analytical tool and also have carried out an analysis of the potential-time curves for reversible and irreversible, stepwise and consecutive processes, with and without kinetic complications. They also suggested the term 'chronopotentiometry'. In an accompanying article, REILLEY, EVERETT AND JOHNS[13] have reviewed the analytical applications of various electrode processes at platinum and mercury pool electrodes. This method has been recently employed by NICHOLSON AND KARCHMER[14] in the determination of lead ion in nitric acid solution. GIERST AND MECHELYNCK[15] have stressed its analytical utility to various practical problems and have demonstrated that, under favorable conditions, determinations can be performed with an accuracy of 0.2%.

More recently the application of chronopotentiometry has been extended to fused salt media also. This method has certain intrinsic advantages over the other methods applicable in such media. It can be applied to the simultaneous *in situ* determination of several ions. Since the time of electrolysis can be made very short, the transport of the ion to the solid inert electrode can be almost ideally regarded as solely due to linear diffusion. The amount of the metal, if deposited as a solid, is very small, and hence there is no interfering dendritic growth into the solution. Furthermore, the deposit can be anodically stripped off and successive determinations can be carried out on the same electrode. The first application was made by LAITINEN AND FERGUSON[17] for the reduction of bismuth, cadmium, silver and cuprous ions at platinum microelectrodes in a solvent which consisted of a eutectic mixture of potassium chloride and lithium chloride at 450°C. These authors used a pen recorder* for the transition time (τ) measurements. It was found that for τ of the order of 2-5 seconds, the theoretical principles of chronopotentiometry[18] were obeyed. From the data for cadmium chloride in this solvent[19], the product of current density, I and $\tau^{1/2}$ was shown to be linear with the cadmium chloride concentration over the range 2.08 to 70 m*M* using different current densities and microelectrodes of different areas and geometries. In all other cases[17] also, over a 10- to 15-fold change in concentration, $I\tau^{1/2}$ values were proportional to the bulk concentration of the depolarizer (C_0). From the slopes of $I\tau^{1/2}$ *vs.* C_0 curves the diffusion coefficient (D) of copper(I), silver, cadmium and bismuth(III) ions were computed to be 3.5, 2.6, 1.7 and $0.6 \cdot 10^{-5}$ cm^2 sec^{-1}. The diffusion coefficient of silver may be compared with the value $4.0 \cdot 10^{-5}$ cm^2 sec^{-1} as reported by DELIMARSKII *et al.*[20] over the concentration range 3-18 m*M* as determined by the variation of the current with time for linear diffusion[21].

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LAITINEN AND FERGUSON's work was limited to τ of the order 2-5 sec. For $\tau > 5$ sec thermal convection interfered, while for $\tau < 2$ sec the measurements were not accurate due to sluggishness of the recorder. It also appeared that a correction for a residual τ, *i.e.* the transition time for the solvent itself must be applied. It became obvious that, in any extension of this study, τ was to be kept as small as possible. Of course, it has to be large enough so that it is much greater than the time needed in charging the double layer at the metal – melt interface. In the present investigation, the transition time was limited to less than one second, and the oscillographic method of recording was adopted. These measurements were also carried out in fused KCl – LiCl at 450°C. While this study was in progress, WOOD[22] presented some results on the oscillographic determination of transition time of the order of 0.001 to 1.0 sec for ferrous chloride in fused $CaCl_2$ – NaCl at 600°C in the concentration range 0.02 to 9.4 mole per cent. Linear diffusion theory was found to be applicable over the concentration range employed, and a diffusion coefficient of $2.36 \cdot 10^{-5}$ cm^2 sec^{-1} was calculated.

The fundamentals of chronopotentiometry for various processes have been developed and verified by a number of workers[1,2,7–11,23], by solving Fick's diffusion equation under appropriate boundary conditions. In general, a quantitative interpretation is possible only if the following conditions are satisfied: (1) the electrolysis current remains constant for the duration of electrolysis, (2) there is no side reaction so that the current is used only for the reduction or the oxidation of the depolarizer, (3) a large excess of the supporting electrolyte is present, (4) diffusion is the sole mode of transport of the depolarizer to the electrode, (5) conditions of semi-infinite linear diffusion prevail, and (6) the concentration of the depolarizer before the electrolysis is uniform throughout the solution.

In practice, to satisfy the above conditions, the current-limiting resistance was several hundred times greater than the cell resistance; the electrolysis was carried out under polarographic conditions, *i.e.*, the migration current was negligibly small, and there was no convection. By keeping the electrolysis time of the order of one second, the diffusion layer thickness was kept very small, and before each measurement the solution concentration was made uniform by stirring.

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* Varian, Model G-10, 50 mV, 1 sec, full scale; the chart speed was increased to 4 i.p.s.

Earlier studies[24] have shown that most of the processes involved in the deposition of metal ions on solid microelectrodes in this medium are reversible and involve only a single reduction step without kinetic complications. For such processes, under the same conditions, the following equations are applicable.

$$C(x,t) = C_{\circ} - \frac{2It^{1/2}}{nF\pi^{1/2}D^{1/2}} \exp\left(-\frac{x^2}{4Dt}\right) + \frac{Ix}{nFD} \operatorname{erfc}\left(\frac{x}{2D^{1/2}t^{1/2}}\right) \quad . . . . (1)$$

using the notation, $\operatorname{erfc} \lambda = 1 - \operatorname{erf} \lambda$, and $\operatorname{erf} \lambda = \frac{2}{\pi^{1/2}} \int_0^{\lambda} \exp(-z^2) dz$.

This equation[1,2,23,25] relates the concentration of the depolarizer at a distance, x, perpendicular to the electrode, after a time t $[= (C_{x,t})]$ with its uniform bulk concentration ($C_{\circ}$), and the current density, I.

For a reversible process, the potential of the indicator electrode is given by the Nernst equation, which for the present case is:

$$E = E^{\circ} + \frac{RT}{nF} \ln \left(C_{\circ} - \frac{2It^{1/2}}{nF\pi^{1/2}D^{1/2}}\right) \quad . . . . (2)$$

The quantity within the parentheses represents the depolarizer concentration at a time t, E° the standard potential of the metal ion-metal couple, n the number of electrons and R, T, F have their usual significance.

After a finite time τ, after the start of electrolysis, the surface concentration has just reached zero. From equation (2) τ is given by[2]:

$$\tau^{1/2} = \frac{nF\pi^{1/2}D^{1/2}C_{\circ}}{2I} \quad . . . . (3)$$

At time τ, the ***transition time***[3,4], the potential of the indicator electrode according to equation (2) would be theoretically infinite. In practice, the potential is so negative that the electrolysis of the medium itself occurs.

Substitution of $C_{\circ}$ from eqn. (3) into eqn. (2) gives

$$E = E_{\text{constant}} + \frac{RT}{nF} \ln (\tau^{1/2} - t^{1/2}), \quad . . . . (4)$$

$$\text{where } E_{\text{constant}} = E^{\circ} + \frac{RT}{nF} \ln \frac{2I}{nF\pi^{1/2}D^{1/2}}$$

EXPERIMENTAL PROCEDURE

Anhydrous cadmium, thallium and lead chlorides were prepared by vacuum desiccation of the A.R. grade salts over anhydrous magnesium perchlorate, and anhydrous cobalt chloride was prepared by dehydrating the salt at about 400°C in a flowing atmosphere of dry hydrogen chloride.

The method employed in the preparation of the solvent has been elaborately described elsewhere[19,26]. The purity of the melt was tested by taking a polarographic residual current with a microelectrode of area 0.0013 cm². Up to a potential of —2.0 V *vs.* Pt reference, the residual current was of the order of 2-3 μA.

The platinum electrodes of different areas and geometry were prepared by sealing appropriate B and S gage wires into Corning 0120 glass. The projected areas were determined accurately by optical micrometry. Electrodes 1, 2, and 3 consisted, respectively, of 26-, 22-, and 18-gage wire sealed into the end of 6 mm tube, flush ground with emery and polished to shiny surface by rubbing with "1/2 Hr metallurgical alumina". The projected areas, being the cross-sectional areas of the wire, were found to be 0.13, 0.335 and 0.81 mm², respectively. Electrodes 4 and 5 were cylindrical electrodes made, respectively, from 26- and 18-gage platinum wires projecting to a distance of 0.648 and 1.107 mm, their total areas being 0.976 and 4.608 mm². Electrode 6 was made from 2 mm thick platinum foil, 2.024 × 1.419 mm, suspended by a thin platinum wire. The working electrode was also made from platinum foil and had an area of 1.52 cm². The reference electrode was a platinum foil in equilibrium with Pt(II) solution in the solvent. This has been shown to be reproducible and non-polarizable. Unless otherwise stated, the Pt(II) concentration was 0.1 *M*.

The experimental arrangement for transition-time measurement was similar to the one used by LAITINEN AND FERGUSON[17] except that the oscillographic method of recording potential-time curve was employed. The constant current from the power supply was kept shorted through dummy resistors. A signal of known amplitude[1] triggered the driven sweep of the oscilloscope. Simultaneously, it activated a relay which applied the constant current between the working and the indicator electrodes. The potential variation of the latter with respect to the platinum reference was applied through the D.C. amplifier of the oscilloscope to the deflection plates. It was so adjusted that the horizontal sweep was started first, and the electrolysis current was switched on after a very small interval. This delay enabled the location of the zero point of the potential-time curve. To measure the time, the X-axis of the C.R.O. was calibrated by feeding a square wave signal of known frequency into the Z modulation input of the scope. With the Y amplifier turned off, the horizontal trace consisted of successive bright spots, the time between a given number of spots being known from the frequency of the Z modulation signal.

The potential-time traces were photographed on 35 mm Kodak Tri X film, and the measurements were made from 4×5″ enlargements. For a given set of conditions four or five transition times were recorded. Before being used for the next transition-time measurement the plated metal was anodically stripped off, and the solution was stirred to make the depolarizer concentration uniform throughout the solution.

RESULTS AND DISCUSSION

Table I gives an estimate of the reproducibility of the transition time measured by the present technique. These were carried out for the following conditions: cadmium chloride concentration = $1.56 \cdot 10^{-5}$ moles cm^{-3}, $I = 1.56 \cdot 10^{-2}$ amp cm^{-2}.

The determination of τ was possible within an accuracy of 2% but since in chronopotentiometry $\tau^{1/2}$ is used, the accuracy in the determination of the latter is about 1.4%.

Residual transition time. LAITINEN AND FERGUSON's work[17] showed that a transi-

TABLE I

Expt. No.	τ, *sec*	$\tau^{1/2}$, *sec*$^{1/2}$
1.	*0.638	*0.799
2.	0.682	0.826
3.	0.693	0.832
4.	0.673	0.820
5.	0.693	0.832
6.	0.717	0.847
7.	0.705	0.840
8.	0.690	0.831
9.	0.695	0.834
10.	0.693	0.832
av.	0.693	0.833 ± 0.014 (std. dev.)

* Not used in calculation of the average.

tion time of the order 0.01-0.09 sec must be assigned to the melt itself. Such a *residual* transition time is not generally observed in aqueous work. In the fused salt medium the concentration of the supporting electrolyte is 25-30 times greater than for a corresponding experiment in aqueous medium so that impurities from the supporting electrolyte are at correspondingly higher levels. Residual hydroxyl ion, water, and silicate contaminations are probably the main causes of residual transition time. In this study, the residual τ was recorded by employing a low current density and a very short time-base of the oscilloscope. A typical potential - time curve for the solvent is shown in Fig. 1. For the potential range of —1.0 to —1.5 V *vs.* 0.1*M* Pt reference, the $I\tau^{1/2}$ value varied from 0.35 — $0.6 \cdot 10^{-2}$ amp cm^{-2} sec$^{1/2}$. It may be pointed out that the residual transition time observed is much greater than the time used in charging the double layer at the Pt/melt interface.

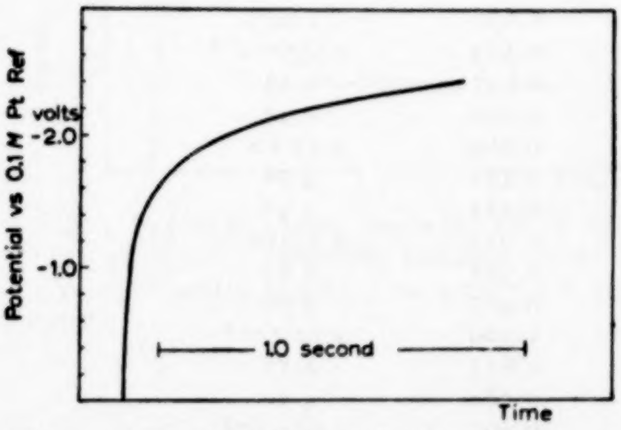

Fig. 1. Potential - time curve for the solvent. The current density was $1.16 \cdot 10^{-2}$ amp cm^{-2}.

Chronopotentiometric study was carried out for the reduction of cadmium, cobalt, lead and thallium chlorides at 450°C. The standard potentials for the metal - metal ion couples at this temperature have been found[27] to be as follows: Cd(II) - Cd, —1.306; Co (II) - Co, —0.984; Pb(II) - Pb, —1.101, and Tl(I) - Tl, —1.480 V *vs.* 1.0*M* Pt(II) - Pt reference.

Fig. 2 is a typical potential-time curve for the reduction of thallium ion at the microelectrode under the conditions: thallium chloride concentration = $1.39 \cdot 10^{-5}$ moles cm^{-3}, $I = 2.037 \cdot 10^{-2}$ amp cm^{-2} (electrolysis current = $165 \cdot 10^{-6}$ amp; area of electrode = 0.0081 cm^{2}).

TABLE II

CHRONOPOTENTIOMETRIC DATA ON CADMIUM CHLORIDE IN KCl-LiCl AT 450°C

C *moles/l*	*I* *amp cm*$^{-2}$	τ_{av} *sec*	$I\tau^{1/2}$ *amp cm*$^{-2}$ *sec*$^{1/2}$	$\frac{I\tau^{1/2}}{C}$ $10^3 \frac{\text{amp cm sec}^{1/2}}{\text{moles}}$	*Electrode*
(a) Linear diffusion upwards to plane electrode					
$2.767 \cdot 10^{-2}$	$4.22 \cdot 10^{-2}$	1.306	$4.85 \cdot 10^{-2}$	*1.75	1
	5.00	1.365	5.85	2.11	
	5.50	1.167	5.94	2.14	
$3.30 \cdot 10^{-2}$	$5.00 \cdot 10^{-2}$	1.986	$7.04 \cdot 10^{-2}$	2.13	1
	5.50	1.54	6.84	2.07	
				av.: 2.11	
				av. dev.: 0.02	
				std. dev.: 0.03	
$1.565 \cdot 10^{-2}$	$4.58_2 \cdot 10^{-2}$	0.088	$1.36 \cdot 10^{-2}$	0.83	2
2.389	4.58_2	0.209	$2.08 \cdot 10^{-2}$	0.87	
$3.30 \cdot 10^{-2}$	$3.98 \cdot 10^{-2}$	0.327	2.28	*0.69	2
	5.00	0.359	2.99*	0.90_5	
	5.50	0.253	2.76	0.83_6	
	5.79	0.196	2.56	0.77_5	
				av.: 0.84_3	
				av. dev.: 0.03	
				std. dev.: 0.04_8	
$2.389 \cdot 10^{-2}$	$2.47 \cdot 10^{-2}$	0.544	$1.83 \cdot 10^{-2}$	0.77	3
	3.722	0.220	1.745	*0.73	
	5.00	0.151	1.945	0.81_4	
$3.154 \cdot 10^{-2}$	$3.716 \cdot 10^{-2}$	0.463	$2.535 \cdot 10^{-2}$	0.80_4	3
	5.00	0.257	2.53	0.80_2	
	6.185	0.226	2.94	*0.93_2	
$4.045 \cdot 10^{-2}$	$4.22 \cdot 10^{-2}$	0.666	$3.43 \cdot 10^{-2}$	0.84_8	3
	5.00	0.451	3.36	0.81_7	
	5.50	0.383	3.40	0.84	
$4.453 \cdot 10^{-2}$	4.22	0.715	$3.57 \cdot 10^{-2}$	0.80_2	3
	5.00	0.588	3.83	0.86_1	
	5.50	0.427	3.59	0.80_6	
$4.897 \cdot 10^{-2}$	$4.22 \cdot 10^{-2}$	1.009	$4.22 \cdot 10^{-2}$	0.86_1	3
	5.00	0.677	4.12	0.84_1	
	5.50	0.582	4.20	0.85_8	
$5.947 \cdot 10^{-2}$	$5.00 \cdot 10^{-2}$	0.991	$4.98 \cdot 10^{-2}$	0.83_8	3
	5.50	0.804	4.94	0.83_1	
	6.00	0.695	4.99	0.83_9	
$7.346 \cdot 10^{-2}$	$6.50 \cdot 10^{-2}$	0.995	$6.48 \cdot 10^{-2}$	0.88_2	3
	7.00	0.724	5.95	0.80_9	
	8.00	0.609	6.24	0.84_9	
				av.: 0.84_2	
				av. dev.: 0.02	
				std. dev.: 0.026	

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* Not used in evaluation of the average.

(Continued on p. 7)

TABLE II

(Continued from p. 6)

C *moles/l*	I *amp cm^{-2}*	τ_{av} *sec*	$I\tau^{1/2}$ *amp cm^{-2} sec$^{1/2}$*	$\frac{I\tau^{1/2}}{C}$ $10^3\,\frac{\text{amp cm sec}^{1/2}}{\text{moles}}$	*Electrode*
(b) Diffusion to foil electrodes					
$1.275 \cdot 10^{-2}$	$1.233 \cdot 10^{-2}$	0.754	$1.07 \cdot 10^{-2}$	0.83_8	6
	1.40	0.597	1.08	0.84_6	
	1.57	0.470	1.07	0.83_8	
	1.742	0.326	1.00	0.78_4	
				av.: 0.826	
				av. dev.: 0.021	
				std. dev.: 0.025	
(c) Diffusion to cylindrical electrodes					
$2.30 \cdot 10^{-2}$	$3.247 \cdot 10^{-2}$	0.477	$2.24 \cdot 10^{-2}$	0.97_2	4
	4.22	0.273	2.21	0.95_9	
	5.00	0.194	2.20	0.96_3	
	5.50	0.170	2.26	0.98_1	
$4.259 \cdot 10^{-2}$	$2.169 \cdot 10^{-2}$	3.400	$3.99 \cdot 10^{-2}$	0.94	5
	3.254	1.411	3.86	0.91	
				av.: 0.95_4	
				av. dev.: 0.026	

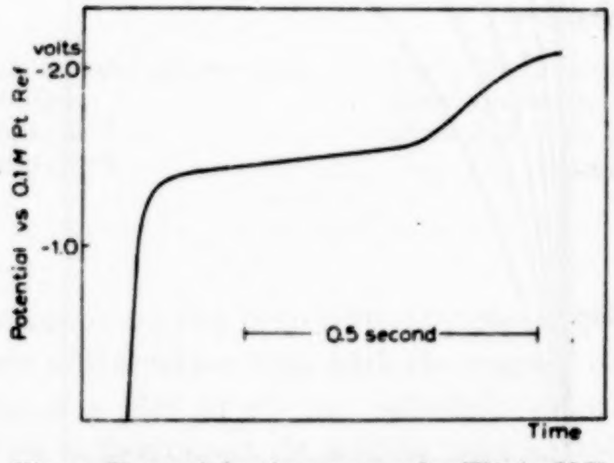

Fig. 2. Potential–time curve for Tl^+ in KCl–LiCl at 450°C. Thallium chloride conc. = $1.39 \cdot 10^{-5}$ moles cm^{-3}; $I = 2.037 \cdot 10^{-2}$ amp cm^{-2}.

The results of transition-time measurements for the reduction of cadmium ion at various current densities and with electrodes of different geometry are presented in Table II. Each value of τ is the average of three or more individual measurements agreeing within 1 to 2%. For different concentrations the values of $I\tau^{1/2}$ are presented. In each case the value of the constant $\frac{I\tau^{1/2}}{C}$, which by analogy to diffusion current constant has been termed[14] the "*transition time constant*", was calculated.

For electrode 6 (foil), in which case the diffusion is very nearly linear and which was made for basis of comparison with other electrodes, the average value of transition time constant was $0.82_6 \cdot 10^3$ amp sec$^{-1/2}$ cm per mole. For electrodes 2 and 3, which are planar with diffusion upwards, the average value of the constant, $0.84_2 \cdot 10^3$, is very close to the above in spite of different areas. Thus in both cases the conditions of semi-infinite linear diffusion are satisfied. However, for electrode 1, which geometrically is similar to 2 and 3 but much smaller in dimensions, the average value of transition time constant, $2.11 \cdot 10^3$, was very high. The positive deviation with respect to linear diffusion means that more of the reducible ions diffuse in than can be accounted for by linear diffusion. To understand this, some calculations were made to determine the variation in the concentration of the reducible ion as a function of the distance from the electrode for various periods of electrolysis. For this purpose equation (1) was used, and a hypothetical case, in which $C_o = 1 \cdot 10^{-5}$ moles cm^{-3}, $n = 2$, $D = 2 \cdot 10^{-5}$ cm^{2}sec^{-1}, was taken. (It will be seen that this value of D is very close to the determined value in this case.) The concentration of the depolarizer for various values of x at the instant when the concentration at the electrode surface is zero or, in other words, when the electrode has just reached a state of virtually complete concentration polarization is shown in Fig. 3.

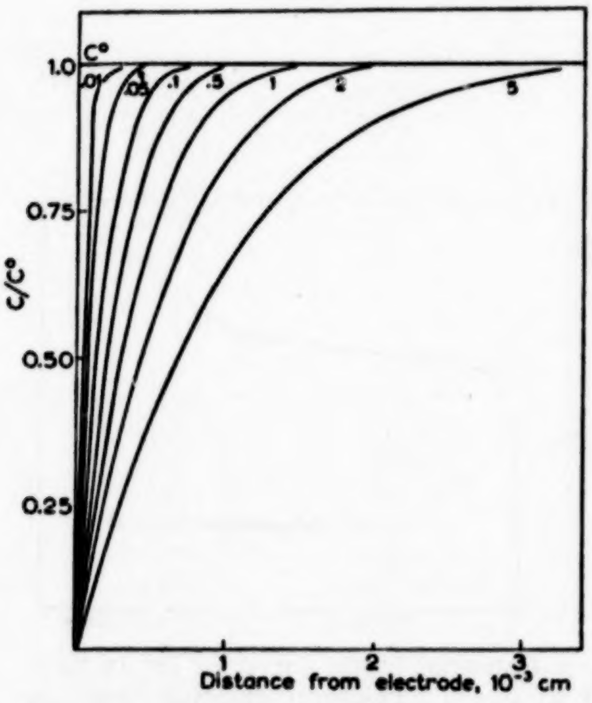

Fig. 3. Theoretical curves for concentration gradients calculated for time of 0.01-5 sec since the beginning of electrolysis. $CdCl_2$ conc. $2.3 \cdot 10^{-5}$ moles cm^{-3}; temp., 450°C.

For this case the diffusion layer thickness, corresponding to a distance at which the concentration is 95% of the bulk concentration, changes markedly with time: for $t =$ 0.05, 1.0, 0.5, 1.0 and 2.0 sec, the diffusion layer thicknesses are 0.024, 0.046, 0.070, 0.100 and 0.143 mm, respectively.

It will be seen that for electrodes 2, 3 and 6, the dimensions of the electrodes are much greater than the diffusion layer thickness so that the mode of diffusion is principally linear. Similarly, for the cylindrical electrodes a considerable portion of the area of the electrode has linear diffusion to it, and hence the response of these electrodes too is comparable to that of 2, 3 and 6, in spite of the different shapes and the areas. However, for electrode 1 where for the particular time used dimensions of the electrode are much smaller and are of the same order as the prevailing diffusion field, it would be more appropriate to regard the diffusion field as hemispherical. This would lead to larger transport of the reducible species to the electrode than accounted for by linear diffusion alone, thus accounting for the positive deviation of the transition time constant which was observed.

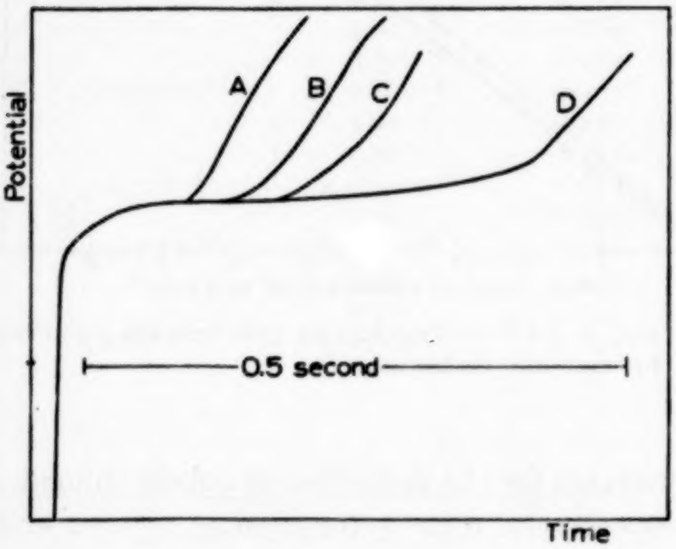

Fig. 4. Effect of electrolysis current on the potential-time curves for cadmium.
A: $I = 6.117 \cdot 10^2$ amp cm^{-2}.
B: $I = 5.00 \cdot 10^2$ amp cm^{-2}.
C: $I = 4.22$.
D: $I = 3.247$.

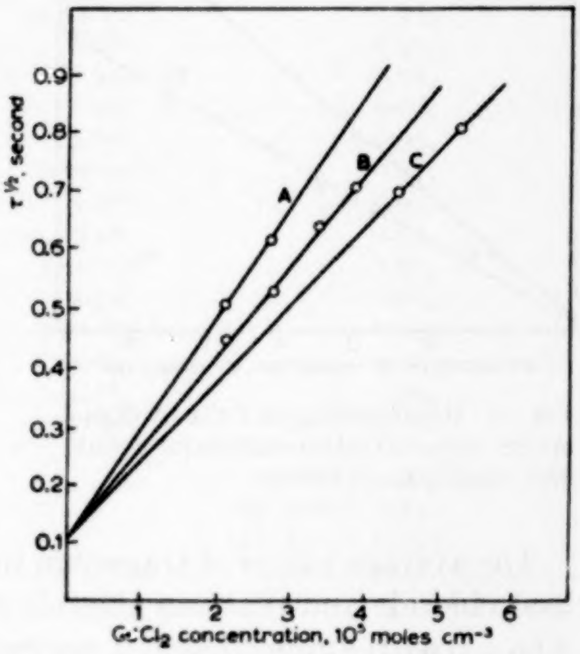

Fig. 5. Variation of $\tau^{1/2}$ with cadmium chloride concentration for different current densities. A, B, C for $4.0, 5.0, 6.0 \cdot 10^{-2}$ amp cm^{-2}.

The applicability of equation (3) has been tested by plotting the different variables. Fig. 4 shows the variation of transition time with the current density for a given concentration, while in Fig. 5 a plot of $\tau^{1/2}$ *vs.* cadmium chloride concentration for different current densities is portrayed. It will be noticed that the plots in Fig. 5 extrapolate to $\tau^{1/2} = 0.11$ sec for zero concentration of the depolarizer, which corresponds to a τ of the order of 0.012 sec for the solvent at a potential corresponding to deposition potential of cadmium. $I \tau^{1/2}$ *vs.* depolarizer concentration plots for cadmium chloride are depicted in Fig. 7. For each point, at least three current densities were used, and for a given current density three or more transition times were recorded. It may be concluded that the theoretical relationship holds good in all the cases. It will be noted that this plot extrapolates to about $0.2 \cdot 10^{-2}$ amp cm^{-2} sec$^{1/2}$ for the zero concentration of the depolarizer. This value is to be ascribed to the solvent. From the slope of $I \tau^{1/2}$ *vs.* C_0 plot, the diffusion coefficient of cadmium ion at 450°C was calculed to be $2.08 \cdot 10^{-5}$ cm^2 sec^{-1}.

Chronopotentiometric studies were also carried out for the reduction of $CoCl_2$, $PbCl_2$ and TlCl (Figs. 6 and 7). From the earlier experience of similar studies for cadmium chloride, only electrode 3 whose response has been shown to approximate closely to a linear diffusion electrode, was used in all the cases. The applicability of equation (3) in all these cases has been found to be good. The data are presented in Tables III to V.

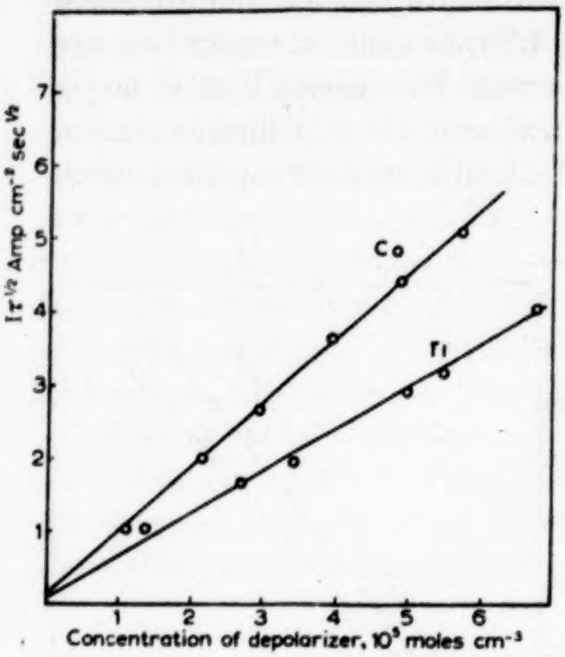

Fig. 6. Relationship of $I\tau^{1/2}$ *vs.* depolarizer concentration curves for cobalt and thallium chlorides.

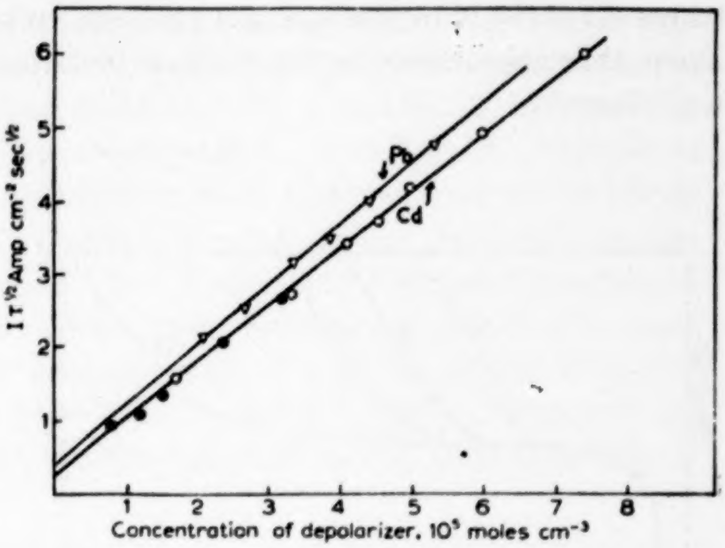

Fig. 7. $I\tau^{1/2}$ *vs.* depolarizer concentration curves for lead and cadmium.

The average values of transition time constants for the reduction of cobalt chloride, lead chloride and thallium chloride are, respectively, 0.90 ± 0.031, 0.95 ± 0.04 and $0.59 \pm 0.02 \cdot 10^3$ amp cm sec$^{-1/2}$ per mole. The diffusion coefficient of these ions calculated from the slopes of $I\tau^{1/2}$ *vs.* depolarizer concentration curves were 2.42, 2.18 and $3.88 \cdot 10^{-5}$ cm^2 sec^{-1}.

TABLE III

CHRONOPOTENTIOMETRIC DATA ON COBALT CHLORIDE IN KCl–LiCl AT 450°C

C *moles/l*	I *amp cm^{-2}*	τ *sec*	$I\tau^{1/2}$ *amp cm^{-2} sec$^{1/2}$*	$\frac{I\tau^{1/2}}{C}$ $\frac{10^3\ \text{amp cm sec}^{1/2}}{\text{mole}}$
$1.143 \cdot 10^{-2}$	$1.481 \cdot 10^{-2}$	0.461	$1.00 \cdot 10^{-2}$	0.87_5
	2.00	0.277	1.05	0.91_8
$2.154 \cdot 10^{-2}$	$2.00 \cdot 10^{-2}$	0.969	$1.96 \cdot 10^{-2}$	0.91_3
	2.50	0.689	2.07	0.96
	3.00	0.479	2.07	0.96
$2.973 \cdot 10^{-2}$	$2.50 \cdot 10^{-2}$	1.075	$2.59 \cdot 10^{-2}$	0.87_1
	3.00	0.711	2.53	0.85
	3.50	0.639	2.79	0.93_7
$3.913 \cdot 10^{-2}$	$3.50 \cdot 10^{-2}$	1.012	$3.51 \cdot 10^{-2}$	0.89_8
	4.00	0.875	3.74	0.95_7
	5.00	0.438	3.31	0.84_7
	5.50	0.384	3.41	0.87_3
$4.87 \cdot 10^{-2}$	$7.665 \cdot 10^{-2}$	0.342	$4.43 \cdot 10^{-2}$	0.90_8
$5.761 \cdot 10^{-2}$	$8.642 \cdot 10^{-2}$	0.370	$5.25 \cdot 10^{-2}$	0.91_1
	9.26	0.292	5.00	0.86_8
			av.:	0.90
			av. dev.:	0.031
			std. dev.:	0.034

TABLE IV

CHRONOPOTENTIOMETRIC DATA ON LEAD CHLORIDE IN KCl–LiCl AT 450°C

C moles/l	I amp cm^{-2}	τ_{av} sec	$I\tau^{1/2}$ amp cm^{-2} sec$^{1/2}$	$\frac{I\tau^{1/2}}{C}$ $\frac{10^3 \text{ amp cm sec}^{1/2}}{\text{mole}}$
$2.113 \cdot 10^{-2}$	$3.50 \cdot 10^{-2}$	0.388	2.18	1.03
	4.00	0.260	$2.04 \cdot 10^{-2}$	0.96
	4.50	0.264	2.32	1.09
	5.00	0.202	2.24	1.05
$2.707 \cdot 10^{-2}$	$3.50 \cdot 10^{-2}$	0.527	$2.54 \cdot 10^{-2}$	0.93_4
	4.00	0.389	2.48	0.91_2
	4.50	0.306	2.49	0.91_6
	5.00	0.284	2.66	0.97_6
	5.50	0.234	2.68	0.90_6
$3.375 \cdot 10^{-2}$	$4.50 \cdot 10^{-2}$	0.471	$3.08 \cdot 10^{-2}$	0.91_1
	5.00	0.411	3.20	0.94_7
	5.50	0.328	3.15	0.93_2
$3.85 \cdot 10^{-2}$	$4.489 \cdot 10^{-2}$	0.612	$3.50 \cdot 10^{-2}$	0.90_9
	5.00	0.496	3.52	0.91_4
$4.414 \cdot 10^{-2}$	$5.50 \cdot 10^{-2}$	0.566	$4.12 \cdot 10^{-2}$	0.93_3
	6.00	0.512	4.29	0.97_1
	6.50	0.415	4.18	0.94_6
$5.28 \cdot 10^{-2}$	$6.00 \cdot 10^{-2}$	0.635	$4.77 \cdot 10^{-2}$	0.90_3
			av.:	0.95_6
			av. dev.:	0.04
			std. dev.:	0.053

TABLE V

CHRONOPOTENTIOMETRIC DATA ON THALLIUM CHLORIDE IN KCl–LiCl AT 450°C

C moles/l	I amp cm^{-2}	τ sec	$I\tau^{1/2}$ amp cm^{-2} sec$^{1/2}$	$\frac{I\tau^{1/2}}{C}$ $\frac{10^3 \text{ amp cm sec}^{1/2}}{\text{mole}}$
$1.39 \cdot 10^{-2}$	$1.259 \cdot 10^{-2}$	0.836	$1.15 \cdot 10^{-2}$	*0.82_8
$2.70 \cdot 10^{-2}$	$1.743 \cdot 10^{-2}$	0.783	$1.53_6 \cdot 10^{-2}$	0.56_8
	2.012	0.592	1.54_8	0.57_3
	2.481	0.479	1.71_6	0.63_5
	3.037	0.362	1.82_8	*0.67_7
$3.456 \cdot 10^{-2}$	$2.185 \cdot 10^{-2}$	0.734	$1.87_6 \cdot 10^{-2}$	0.54_1
	2.469	0.644	1.98_3	0.57_3
	3.012	0.378	1.85_7	0.53_6
$4.961 \cdot 10^{-2}$	$3.037 \cdot 10^{-2}$	0.868	$2.83 \cdot 10^{-2}$	0.57_1
	3.518	0.640	2.82	0.57_1
	3.901	0.562	2.92	0.58_9
$5.469 \cdot 10^{-2}$	$3.543 \cdot 10^{-2}$	0.773	$3.12 \cdot 10^{-2}$	0.57_0
	3.908	0.649	3.16	0.57_8
	4.506	0.509	3.20	0.58_5
$6.752 \cdot 10^{-2}$	$4.518 \cdot 10^{-2}$	0.843	$4.14 \cdot 10^{-2}$	0.61_1
	4.975	0.680	4.13	0.61_1
	5.358	0.460	4.16	0.61_4
	6.00	0.560	4.07	0.60_2
$7.818 \cdot 10^{-2}$	$6.00 \cdot 10^{-2}$	0.654	$4.85 \cdot 10^{-2}$	0.61_8
	6.47	0.523	4.68	0.59_8
	7.018	0.356	4.19	0.53_5
			av.:	0.588
			av. dev.:	0.024
			std. dev.:	0.029

SUMMARY

Previous work in the application of chronopotentiometry in aqueous and fused salt media has been reviewed. This investigation describes the application of this principle to the reduction of cadmium, cobalt, lead and thallium ions in a fused eutectic mixture of potassium chloride and lithium chloride at 450°C. Platinum microelectrodes of different areas and geometry were used. The transition time was limited to the order of 0.2 to 0.7 sec using oscillographic recording. It was found that so long as the dimensions of the electrode were considerably greater than the thickness of the diffusion, layer, linear diffusion theory was obeyed. The transition time constants for cadmium, cobalt, lead and thallium ions were found to be 0.83 ± 0.02, 0.90 ± 0.03, 0.95 ± 0.04, and $0.59 \pm 0.02 \cdot 10^3$ amp cm $\text{sec}^{1/2}$ per mole, respectively. The diffusion coefficients of these ions were calculated to be 2.08, 2.42, 2.18 and $3.88 \cdot 10^{-5}$ $\text{cm}^2\,\text{sec}^{-1}$, respectively.

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DISCUSSION

Prof. P. Delahay (Baton Rouge):

I am delighted to see this beautiful work of Prof. Laitinen and his coworkers and particularly the application of chronopotentiometry to fused salts.

I should like to point out that treatments of the transition time for spherical and cylindrical electrodes are available. The conditions under which the treatment for linear diffusion can be applied with good accuracy to spherical and cylindrical electrodes can be derived in terms of the transition time and the radius of the electrode.

Prof. H. A. Laitinen:

In addition to geometric conditions, an important limitation is the occurrence of convection, which in principle must occur in non-linear diffusion because of density gradients unless the transition time is very short, and therefore the diffusion layer is very thin. It is, therefore, necessary to determine by experiment the proper experimental conditions.

Prof. P. Delahay:

It is true that experiment is the ultimate criterion, but the theory is a good guide. In fact, I would not be surprised if the condition related to electrode curvature is more stringent than that for convection for electrodes of small diameter.

Dr. H. GERISCHER (Stuttgart):

Es würde mich interessieren, ob die Begrenzung der Transitionszeit nach kurzen Zeiten hin, durch die Wirkungen der Oberflächenrauhigkeit, eine Rolle spielt. Diese Grenze wird an festen Elektroden nimmer dann erreicht, wenn die Dicke der Diffusionsschicht in die Grössenordnung der Rauhigkeits-Höhenunterschiede kommt, und wirkt sich in einem Anstieg des Produktes $I\,\tau^{1/2}$ aus.

PROF. H. A. LAITINEN:

The effect of roughness depends to some extent upon the nature of the metal being deposited. The electrode actually becomes smoother with the deposition of a liquid metal, and rougher with the deposition of a high melting metal. The platinum electrodes were polished with alumina to a mirror surface.

Prof. P. DELAHAY:

In connection with Dr. GERISCHER's remark, I might add that it is not even possible to define a transition time for a rough electrode because the concentration of reducible (or oxidizable) species does not drop to zero at the same moment for different parts of the electrode because of differences in the rate of diffusion. As a result, there is a progressive variation of potential in the transition time range rather than a rapid change of potential. This distortion becomes more pronounced as the transition time becomes shorter.

Prof. H. A. LAITINEN to Prof. N. IBL (Zürich):

The question of cylindrical or spherical diffusion does not enter into the present discussion, because conditions were adjusted to attain linear diffusion.

Prof. F. ČŮTA (Prague):

What was the influence of temperature on the accuracy of the results? Was the melt quiet?

Prof. H. A. LAITINEN:

A temperature control of ± 1° was used in the present study. A variation of ± 2% in transition time, or 1.4% in concentration was observed.

Between each experiment, the solution was stirred, and allowed to become stationary.

Prof. I. M. KOLTHOFF (Minneapolis):

It is interesting that in the fused salt an electro-reduction of the hydroxyl ion to the oxygen ion is obtained. Is it possible to get some quantitative information on the acid character of the hydroxyl ion from the current–potential curves?

Prof. H. A. LAITINEN:

In principle, it is possible to observe a reversible deposition of hydrogen from hydroxyl ion. In the present work, solutions of hydroxyl ion were not stable, because of the use of glass or silica vessels.

Prof. N. IBL (Zürich):

May I ask you if you have also used electrodes in intermittent contact with the melt of the kind employed by LYALIKÓV and by HILLS, INMANN and YOUNG?

Prof. H. A. LAITINEN:

We have not used such electrodes, although they may yield more reproducible results than ordinary stationary microelectrodes. I feel that chronopotentiometry is more exact than such a technique. Our main purpose in running polarographic curves was to establish the oxidation states and to get some idea of the electrode potentials.

AMPÉROMÉTRIE AVEC DEUX ÉLECTRODES INDICATRICES

par

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APERÇU HISTORIQUE

En 1897 SALOMON[1,2] fut le premier à utiliser dans l'argentométrie l'ampérométrie avec deux électrodes indicatrices et, peu après NERNST ET MERRIAM[3] appliquèrent la même méthode à l'acidimétrie.

Après une période d'oubli, en 1926, FOULK ET BAWDEN[4], généralement considérés comme les auteurs, remirent cette méthode en vogue pour l'iodométrie. Le terme fréquemment employé ,,dead stop" doit son origine à leur publication. Mais la divulgation de ce procédé ne date que de 1943, lorsque WERNIMONT ET HOPKINSON[5] en introduisirent l'usage pour le dosage de l'eau selon K. FISCHER[6].

Quant à l'aspect théorique, c'est DELAHAY[7] qui signala le premier que l'allure de la courbe de titrage s'explique à l'aide des courbes de polarisation.

MODE OPÉRATOIRE

Le circuit électrique est très simple: un dispositif potentiométrique permet d'imposer via un galvanomètre une tension constante entre deux électrodes identiques (Fig. 1). Généralement ces électrodes sont en platine poli.

En agitant la solution à une vitesse constante, on mesure l'intensité du courant comme fonction du volume du réactif ajouté.

Pendant l'électrolyse il se fait un transport vers les électrodes et inversement, par suite de la diffusion et aussi de la convection, celui-ci due à l'agitation de la solution. On peut supprimer l'influence de la migration par l'addition d'un électrolyte de base suffisamment concentré. Le nombre des particules déchargées aux électrodes, est le plus souvent petit en comparaison de la quantité, présente dans la solution.

L'intensité du courant d'électrolyse s'exprime par l'équation suivante:

$$i = k\,({}^{*}C - {}^{\circ}C).$$

${}^{*}C$ = concentration dans la masse de la solution.
${}^{\circ}C$ = concentration au voisinage immédiat de l'électrode.
k = constante, dépendant du coefficient de diffusion, de la vitesse de l'agitation et des dimensions des électrodes[8].

Je traiterai successivement des points suivants:

1. Explication qualitative du procédé;
2. Déduction mathématique de la forme idéale de la courbe de titrage, suivie de sa vérification expérimentale;

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3. Exposé succint des titrages déjà publiés;
4. Nouvelles applications.

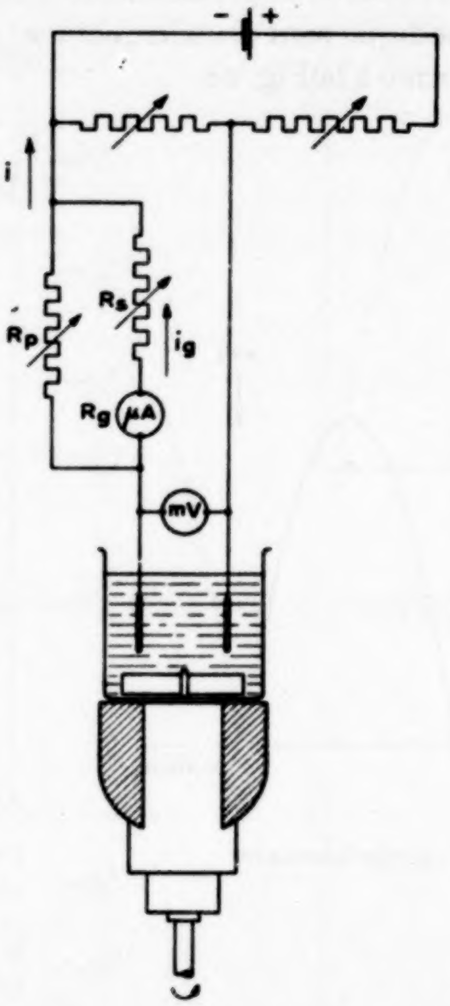

Fig. 1. Appareil, destiné à l'ampérométrie à deux électrodes indicatrices.

1. Explication qualitative

1.1. Je prendrai comme premier exemple le titrage du ferrocyanure avec le bromate dans une solution acidifiée de bromure.

Il est très facile d'esquisser à chaque moment du titrage l'allure de la courbe de polarisation.

Ceci a été fait quatre fois (Fig. 2), à savoir:
(a) avant l'addition du réactif;
(b) lorsque la moitié du réactif est ajoutée;
(c) au moment précis du point équivalent;
(d) après le point équivalent.
(Quant à la notation des coördinates, j'ai suivi la convention polarographique.)

En cas de coïncidence partielle de la courbe de polarisation avec l'abscisse (axe de potentiel), la faible tension △ (± 10 mV) entre les deux électrodes identiques ne suffit pas à provoquer l'électrolyse. Le galvanomètre marque donc zéro. Telle est la situation pour les polarogrammes (a) et (c). Au contraire, les polarogrammes (b) et (d) sont tels, qu'il faut se produire l'électrolyse, parce que, ici, les deux composants conjugués d'un système rédox réversible (ou rapide) sont simultanément présents. Alors le spot du galvanomètre dévie. Le potentiel de l'anode et celui de la cathode sont alors un peu plus élevés respectivement un peu plus faibles que le potentiel d'équilibre représenté par le point d'intersection de la courbe de polarisation et de l'abscisse. Il est évident que les courants anodique et cathodique sont numériquement égaux. L'allure de la courbe de titrage doit donc être conforme à la Fig. 2e.

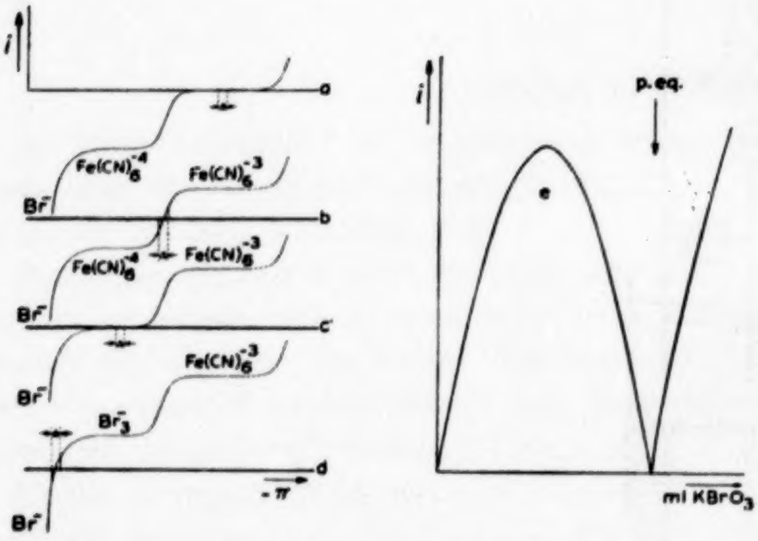

Fig. 2. Titrage de ferrocyanure avec du bromate en milieu acide bromhydrique.

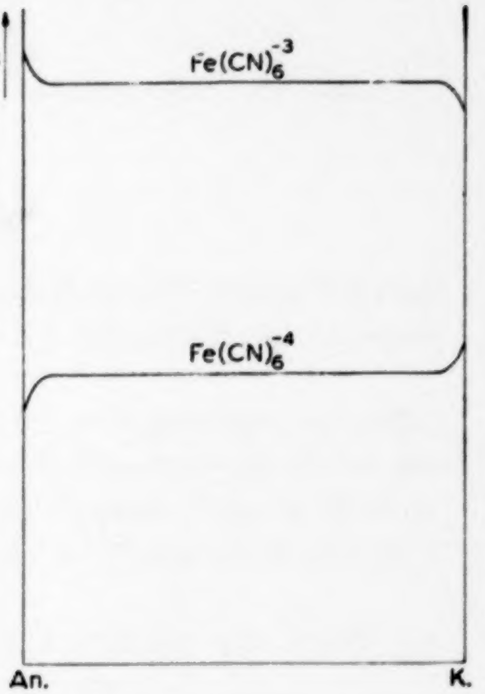

Fig. 3. Concentrations entre l'anode (An.) et le cathode (K.) du ferrocyanure et du ferricyanure, quand le titrage est avancé jusqu'à deux tiers.

La concentration du ferrocyanure ainsi que celle du ferricyanure entre les électrodes au moment que le titrage est avancé jusqu'à deux tiers du point équivalent, sont représentées dans la Fig. 3.

Pendant l'électrolyse la composition ne subit aucun changement (si petit que celui soit), les phénomènes anodique et cathodique étant parfaitement symétriques. Ceci présente un avantage en comparaison de l'ampérométrie classique, surtout en ces cas où le volume est petit et la concentration faible.

1.2. Un deuxième exemple est fourni par la réduction du ferricyanure par l'arsénite en milieu alcalin. Ici sont présents, après le point équivalent, les deux composants conjugués d'un système rédox irréversible (ou lent), de sorte que la courbe de polarisation coïncide partiellement avec l'abscisse. La faible tension imposée ne permet pas l'électrolyse. La Fig. 4 se rapporte à ce titrage.

1.3. Le titrage inverse, à savoir celui de l'arsénite avec le ferricyanure est expliqué dans la Fig. 5.

1.4. Beaucoup de ferrocyanures sont, comme on le sait, très peu solubles tandis que la solubilité des ferricyanures correspondants est meilleure. Comme, en outre, le ferricy-

anure et le ferrocyanure forment ensemble un couple rédox rapide, nous sommes en mesure de titrer avec du ferrocyanure étalonné divers cations, tels que l'ion Zn^{+2},

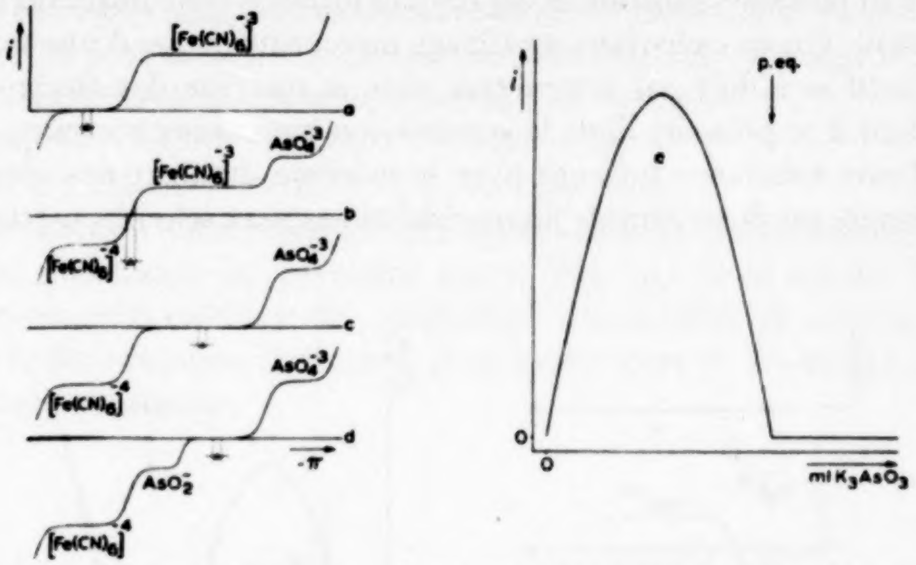

Fig. 4. Titrage de ferricyanure avec de l'arsénite en milieu alcalin.

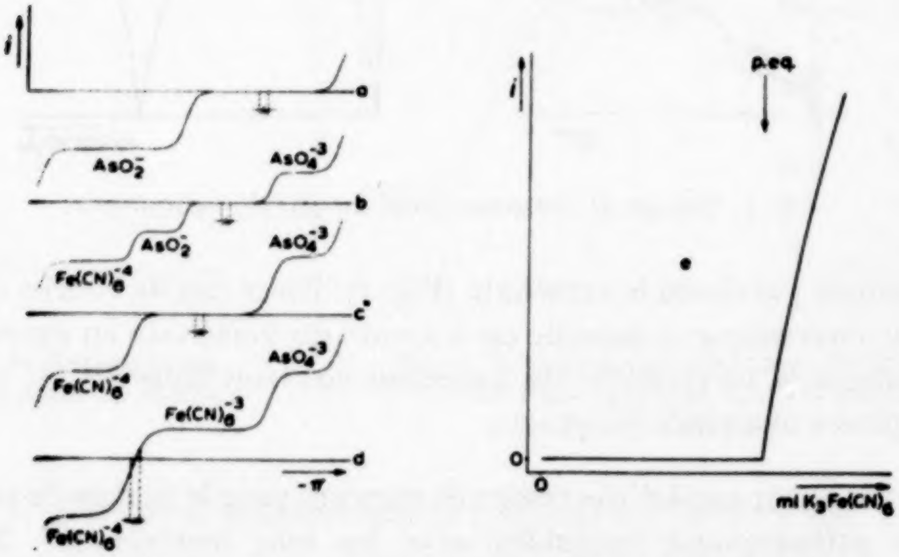

Fig. 5. Titrage d'arsénite avec du ferricyanure.

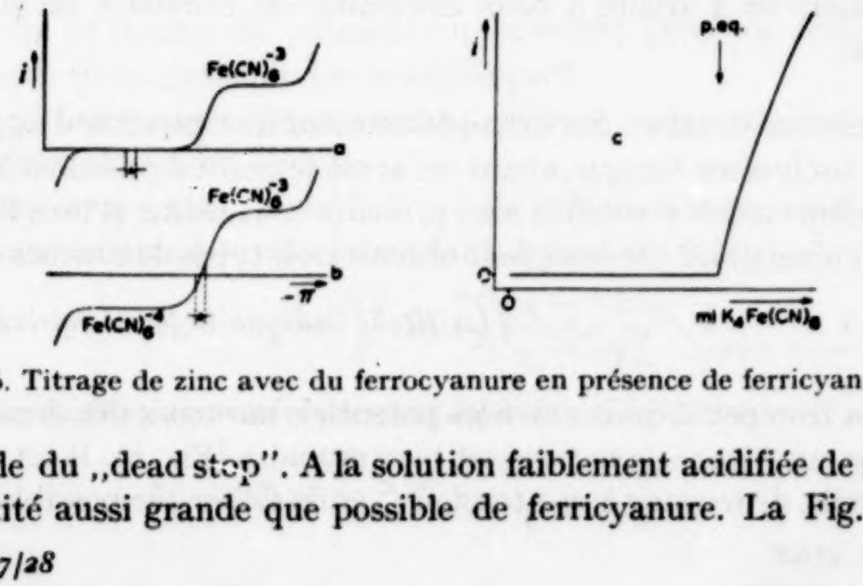

Fig. 6. Titrage de zinc avec du ferrocyanure en présence de ferricyanure.

selon la méthode du ,,dead stop". A la solution faiblement acidifiée de zinc on ajoute alors une quantité aussi grande que possible de ferricyanure. La Fig. 6 montre les

courbes de polarisation que l'on pourrait enregistrer avant (a) et après (b) le point équivalent, ainsi que la courbe de titrage (c).

1.5. On connaît plusieurs substances organiques formant des complexes stables avec le mercure divalent. Or, en exécutant un titrage mercurimétrique d'une telle substance, l'excès du réactif se réduit par interaction avec le mercure des électrodes. Après le point équivalent il se présente donc le système ion mercureux/mercure, lequel est réversible[9,10]. Toute substance formant avec le mercure divalent des complexes d'une stabilité suffisante est donc titrable mercurimétriquement selon la méthode du ,,dead stop''.

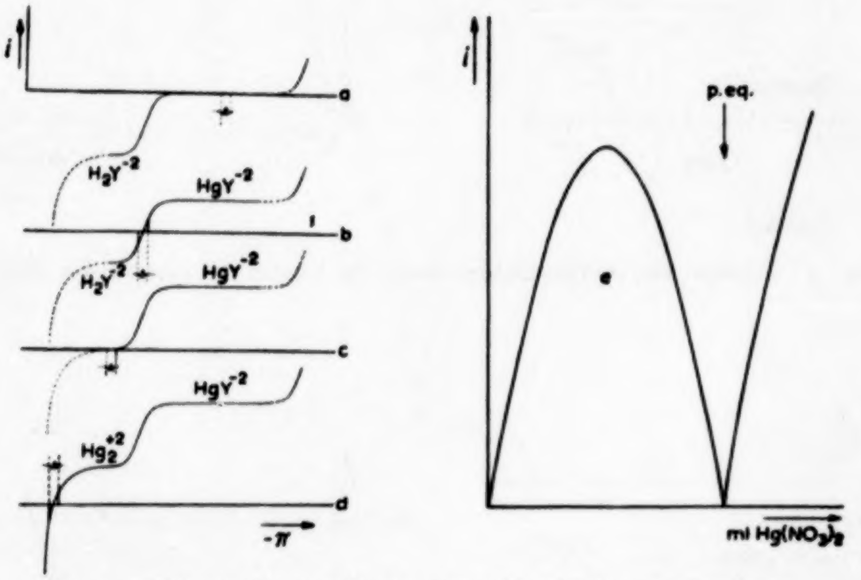

Fig. 7. Titrage de versénate avec du nitrate mercurique.

Comme exemple j'ai choisi le versénate (Fig. 7). En ce cas, la courbe de polarisation d'une solution mercurique, à laquelle on a ajouté du versénate en excès (donc HgY^{-2} + H_2Y^{-2}), indique la réversibilité du processus électrolytique[11,12]. Il en est ainsi de tous les complexes examinés jusqu'ici.

1.6. On peut se servir aussi d'électrodes de mercure pour le titrage de substances donnant des sels suffisamment insolubles, avec les ions mercureux[13]. Après le point équivalent il se présente le système réversible ion mercureux/mercure et par conséquent un courant électrolytique. On observe également un courant avant le point équivalent, mais alors on a affaire à deux électrodes de référence de mauvaise qualité pour ainsi dire.

1.7. Nous pouvons conclure des exemples cités qu'il est possible d'appliquer cette méthode électro-analytique lorsque, avant ou après le point équivalent, les deux composants d'un système rédox réversible sont présents et de même si tous les deux systèmes impliqués sont réversibles. On peut donc obtenir trois types de courbes de titrage:

╲↓__, __↓╱ et ╲↓╱ *(La flèche indique le point équivalent).*

Quand il y a trop peu d'écart entre les potentiels normaux des deux systèmes rédox impliqués dans un titrage, la netteté est bien moindre (Fig. 8). Il est recommandable, en des cas pareils, de recourir à une tension △ aussi faible que possible[14]. En général, la valeur de la tension imposée est de peu d'importance; au contraire, dans l'ampérométrie classique la tension est comprise entre deux limites.

1.8. Dans les exemples cités les réactions anodique et cathodique s'expriment par la même équation. On peut se figurer le cas que pendant l'électrolyse il se produise aux deux électrodes des réactions entièrement différentes, par exemple[15],
à l'anode: $2\,NH_2OH + 6\,OH^- \rightarrow N_2O_2^{-2} + 6\,H_2O + 4e$
et à la cathode: $2 \times (H_2O_2 + 2\,OH^- \leftarrow O_2 + 2\,H_2O + 2e)$.

La vitesse de réaction entre l'oxygène et l'hydroxylamine étant minime, il se produit à leur présence simultanée un potentiel mixte (Fig. 9a). Il en résulte la possibilité de titrer au moyen de la méthode du ,,dead stop'' une solution de méthanal exposée à l'air avec de l'hydroxylamine étalonnée. Il se forme alors de l'oxime. La Fig. 9b représente la courbe de titrage.

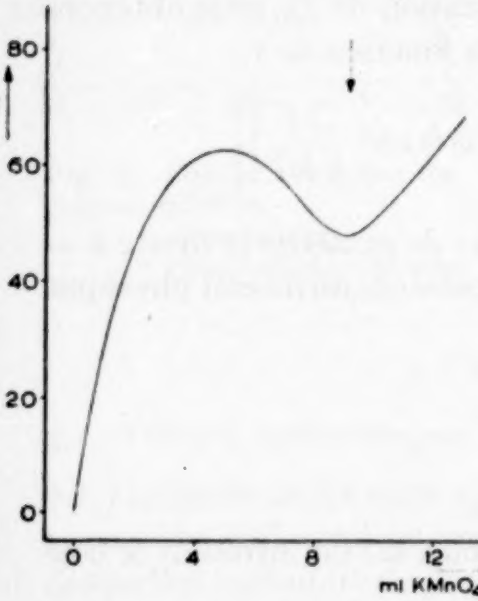

Fig. 8. Titrage de ferrocyanure avec du permanganate en milieu alcalin.

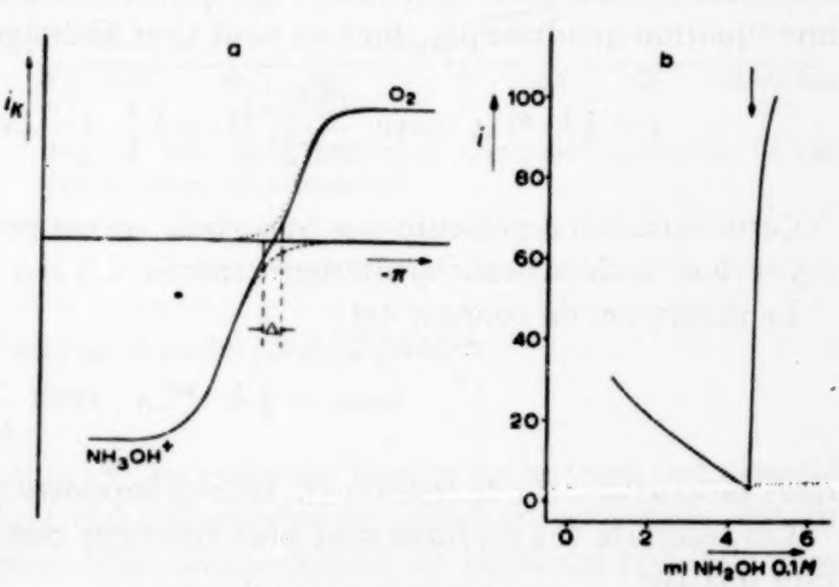

Fig. 9. Titrage de méthanal avec de l'hydroxylamine.
a. Polarogramme après le point équivalent,
b. courbe de titrage.

2. *Déduction mathématique et vérification expérimentale*

Comme les expériences par des systèmes réversibles s'effectuent plus rapidement que par les systèmes irréversibles, je me suis borné aux premiers[16,17,18]. GAUGUIN ET CHARLOT[19] ont déduit une équation généralement valable. Leur point de départ, notamment l'équation de la courbe de polarisation, présente alors une forme différente, déduite de la théorie de la cinétique électrochimique[20].

Je ne traiterai ici brièvement que la courbe de titrage jusqu'au point équivalent du dosage oxidimétrique du ferrocyanure.

La polarographie nous renseigne sur la forme du polarogramme. Voici l'équation du potentiel cathodique comme fonction du courant cathodique[21]:

$$\pi_K = \pi_o + \frac{RT}{F} \ln \frac{{}^*C_{Ox} - i/k_{Ox}}{{}^*C_R + i/k_R}$$

Pour un courant anodique numériquement égal on a l'équation:

$$\pi_{An} = \pi_o + \frac{RT}{F} \ln \frac{{}^*C_{Ox} + i/k_{Ox}}{{}^*C_R - i/k_R}$$

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Par soustraction on obtient pour la tension entre les électrodes:

$$\triangle = \frac{RT}{F} \ln \frac{({}^*C_{\mathrm{Ox}} + i/k_{\mathrm{Ox}}) \cdot ({}^*C_{\mathrm{R}} + i/k_{\mathrm{R}})}{({}^*C_{\mathrm{R}} - i/k_{\mathrm{R}}) \cdot ({}^*C_{\mathrm{Ox}} - i/k_{\mathrm{Ox}})}$$

Supposons, dans un cas idéal, que cette tension reste constante.

Mettons:

$${}^*C_{\mathrm{Ox}} = x \cdot {}^*C_{\mathrm{A}} \quad \text{et} \quad {}^*C_{\mathrm{R}} = (1 - x)\, {}^*C_{\mathrm{A}}\,,$$

x: degré d'avancement du titrage,
${}^*C_{\mathrm{A}}$: concentration initiale du ferrocyanure, et pour simplifier:

$$k_{\mathrm{Ox}} = k_{\mathrm{R}} = k.$$

En faisant entrer par substitution ces relations dans l'équation de $\triangle$, nous obtenons une équation quadratique, dont on peut tirer aisément i en fonction de x:

$$i = \tfrac{1}{2}\, k \cdot {}^*C_{\mathrm{A}} \cdot \coth \frac{\triangle F}{2\,RT} \left[1 - \sqrt{\left\{1 - 4x(1-x)\tanh^2 \frac{\triangle F}{2\,RT}\right\}}\right].$$

Cette équation représente une hyperbole, ayant pour axe de symétrie la droite $x = 0.5$ et dont seule la branche inférieure entre $x = 0$ et $x = 1$ présente un interêt physique.

Le maximum de courant est:

$$i_{\max} = \tfrac{1}{2}\, k \cdot {}^*C_{\mathrm{A}} \cdot \tanh \frac{\triangle F}{4\,RT}\,,$$

donc proportionnel à la tension $\triangle$, celle-ci supposée petite.

Les résultats des mesures sont plus aisément comparables si l'on introduit le courant relative

$$j = \frac{i}{i_{\max}}.$$

C'est surtout pour les petites valeurs de la tension ($\triangle$ n'excédant pas une dizaine de millivolts), que j dépend pour très peu de $\triangle$.

L'équation déduite de la sorte pour le courant relative a été confirmée expérimentalement[22]. Alors trois corrections ont dû être apportées aux observations:

(a) Contrairement à la pratique normale, dans cette série d'expériences la tension $\triangle$ aux électrodes a été maintenue autant que possible constante (contrôlée au millivoltmètre électronique), de sorte qu'il n'a plus fallu qu'une correction concernant la chute ohmique dans la solution $i_0 r$, laquelle réduite autant que possible par une forte concentration de l'électrolyte de base; donc:

$$\triangle_{\text{corrigée}} = \triangle_{\text{mesurée}} - i \cdot r.$$

(b) Correction pour la réduction du courant mesuré i à la valeur que l'on devrait mesurer à une tension standardisée:

$$i_{\text{corrigé}} = i_{\text{mesuré}}\; \frac{\triangle_{\text{standard}}}{\triangle_{\text{corrigée}}}$$

(c) Pour éliminer l'effet de la dilution, il faut encore multiplier $i_{\text{corrigé}}$ par: $\left(1 + \dfrac{V_{\mathrm{R}}}{V_{\mathrm{O}}}\right)$, où

V_{O} = volume initial et
V_{R} = volume du réactif ajouté.

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Il ressort de la Fig. 10 que les expériences ont corroboré la théorie. On y voit aussi que la courbe non corrigée donne en fait une indication plus nette du point final et particulièrement en pratique normale la netteté de l'indication devient encore plus accentuée.

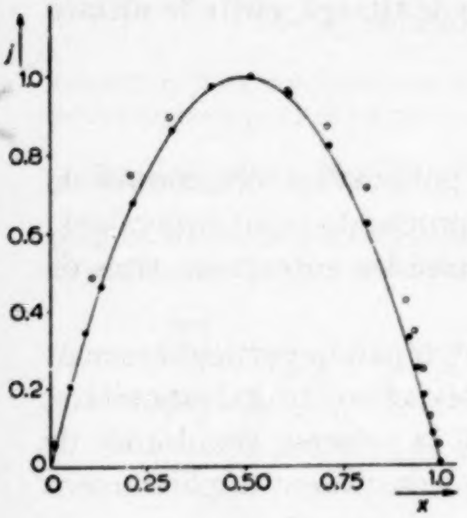

Fig. 10. Courbe théorique du courant relative.
° observations.
• observations corrigées.

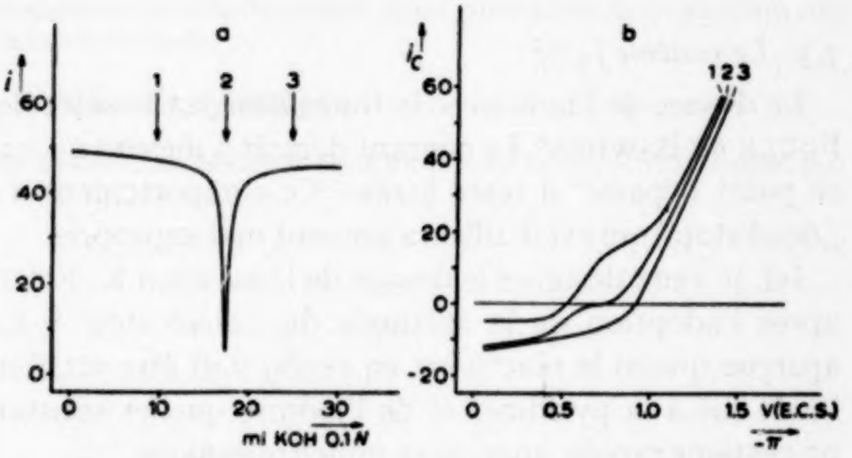

Fig. 11. Un acide titré avec une base; courbe de titrage (a) et polarogrammes (b).

3. *Exposé succint des titrages déjà publiés*

3.1. *Titrages acidimétriques*

3.1. (a) Méthode Nernst et Merriam[3]. Au cours du titrage les auteurs ont observé le courant d'électrolyse employant deux électrodes de palladium palladiées, autour desquelles barbotait de l'hydrogène. Nous avons obtenu de meilleurs résultats avec des électrodes en platine platiné. La courbe de titrage correspond avec l'allure des courbes de polarisation, ce qui ressort des Figs. 11.

3.1. (b) Application d'un indicateur électrométrique. L'addition de faibles quantités de certaines substances[23,24] provoque un changement subit du courant tout près du point équivalent. Parmi les substances proposées l'eau oxygénée s'est avérée la plus appropriée. En milieu alcalin la réaction électrochimique présente malgré la complication du mécanisme le caractère de réversibilité[25] (Fig. 12).

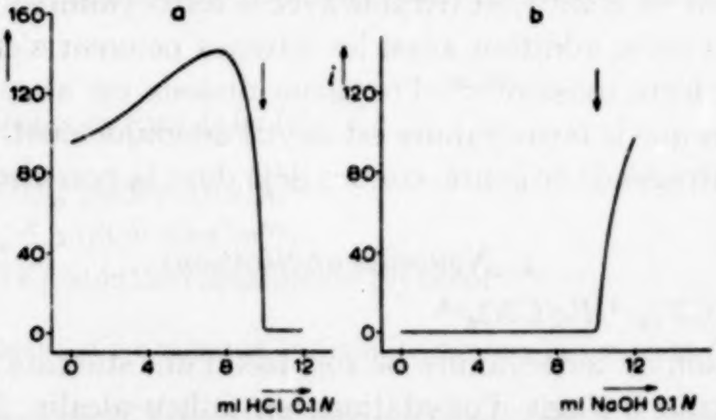

Fig. 12. L'eau oxygénée comme indicateur électrométrique.
(a) Titrage de soude avec de l'acide.
(b) Titrage d'acide avec de la soude.

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3.2. Les systèmes Ag^+/Ag *et* Hg_2^{+2}/Hg

Quand on se sert d'une paire d'électrodes en argent on peut effectuer la détermination de l'ion chlorure[26–28]. On connaît aussi l'emploi d'électrodes en argent partiellement chlorées[29]. Le mercure, remplissant deux creux dans le fond du récipient, forme d'excellentes électrodes[13]. Dans ce cas on a le choix, pour le titrage, entre le nitrate mercureux et le nitrate d'argent.

3.3. Le système J_3^-/J^-

Le dosage de l'iode avec le thiosulfate est le sujet de la publication bien connue de FOULK ET BAWDEN[4]. Le courant décroît à mesure qu'on approche du point équivalent; ce point dépassé, il reste à zéro. Ce comportement a inspiré les auteurs au titre de ,,dead stop" qui est d'ailleurs souvent mal approprié.

Ici, je veux désigner le dosage de l'eau selon K. FISCHER[6], répandu particulièrement après l'adoption de la méthode du ,,dead stop"[5]. La déviation du galvanomètre, aperçue quand le réactif est en excès, doit être attribuée à la présence simultanée de l'iode (lié à la pyridine) et de l'iodure, quelles substances constituent apparemment un système rapide, aussi en ce milieu organique.

3.4. Le système Br_3^-/Br^-

On peut effectuer les titrages de quelques substances inorganiques telles que l'arsénite, l'antimonite[30], l'ion thalleux[31] et l'hydrazine[32] et aussi la bromuration de plusieurs substances organiques[33–36], p.ex. l'aniline et ses dérivés.

3.5. Le système Fe^{+3}/Fe^{+2}

Bien que ce couple rédox ne soit pas tout réversible à la température ambiante[37], il peut néanmoins être utile quand on applique des tensions de 200 mV environ. On connaît les exemples suivants: dosage de $Cr_2O_7^{-2}$ [38], VO_3^- [39,40] et Ce^{+4} [40].

3.6. Le système NO_2/NO_2^-

Grâce au comportement électrochimique d'ailleurs compliqué du système NO_2/NO_2^- [41,42], il est possible de titrer une solution acidifiée d'une amine aromatique avec du nitrite [43,44].

3.7. Titrages par précipitation d'un ferrocyanure

Comme nous avons vu le Zn^{+2} est titrable avec le ferrocyanure. On y ajoute alors du ferricyanure[18]. Sans cette addition aussi les titrages peuvent s'effectuer moyennant l'application d'une forte tension[45,46]; l'oxygène dissous est alors réduit cathodiquement à même temps que le ferrocyanure est oxydé anodiquement. Sans doute on peut exécuter d'autres titrages de ce genre, connus déjà dans la potentiométrie.

4. Nouvelles applications

4.1. Le système $Fe(CN)_6^{-3}/Fe(CN)_6^{-4}$

Quoique la solution de ferricyanure ne soit pas d'une stabilité illimitée, son emploi est avantageux quand il s'agit d'oxydations en milieu alcalin. Nombre de titrages étaient déjà connus dans la potentiométrie. Comme on s'y attendait absolument, ils peuvent être réalisés aussi par la méthode en question.

4.1. (a) Courbes de titrage du type de la Fig. 2.

$Ce(CO_3)_2^{-1} \rightarrow Ce(CO_3)_2$, solution saturée de potasse[47];
$Co(NH_3)_6^{+2} \rightarrow Co(NH_3)_6^{+3}$, solution ammoniacale[48];
$Co(en)_3^{+2} \rightarrow Co(en)_3^{+3}$, solution tamponnée d'éthylènediamine[49];
$2\,J^- \rightarrow J_2$, solution acidifiée, contenant du Zn^{+2} [50];

formation d'un précipité avec le ferrocyanure formé; dépassé le point équivalent, le courant revient probablement par l'oxydation consécutive de l'iode.

$Mn(CN)_6^{-4} \rightarrow Mn(CN)_6^{-3}$ [51], solution de cyanure;

pour les solutions très concentrées de cyanure les résultats sont un peu en excès, probablement par oxydation du cyanure ou du platine (Fig. 13).

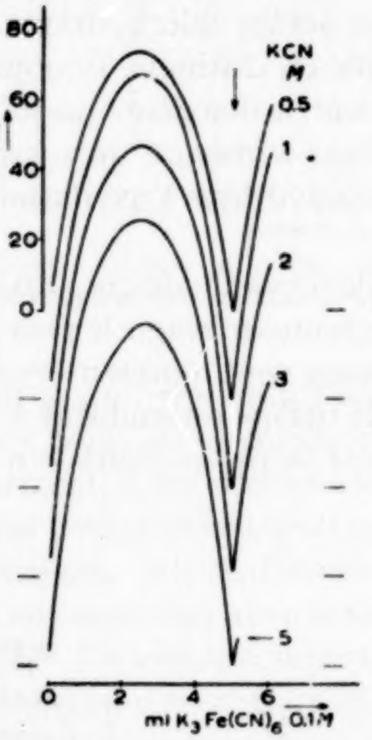

Fig. 13. Titrage de manganèse avec du ferricyanure en présence de cyanure en concentration indiquée.

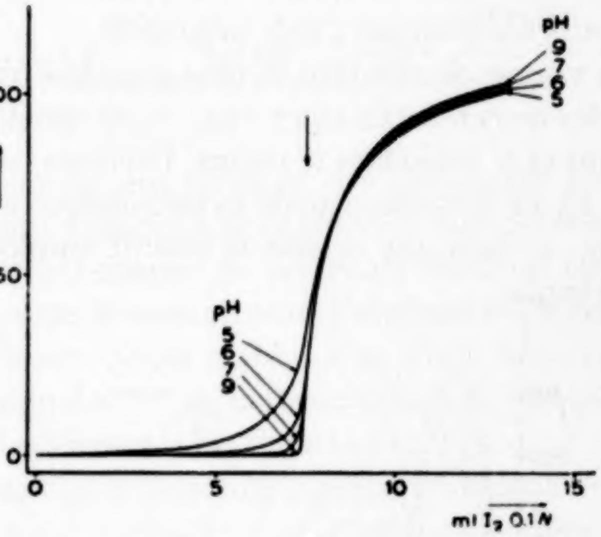

Fig. 14. Titrage de cyanure avec de l'iode.

4.1. (b) Courbes de titrage du type de la Fig. 4. Ces courbes se présentent dans la détermination du ferricyanure avec de l'arsénite[22] ou du nitrate mercureux[52] en solution alcaline.

4.1. (c) Courbes de titrage du type de la Fig. 5.

$Tl^+ \rightarrow Tl(OH)_3$, milieu alcalin[53];
$AsO_2^- \rightarrow AsO_4^{-3}$, milieu alcalin[54];
$Mn(II) \rightarrow Mn(IV)$, solution alcaline de glycérol[55];

dépassé le point équivalent, il y a manque de stabilité par oxydation lente du glycérol.

4.2. Le système J_3^-/J^-

4.2. (a) Dosage d'iode. L'iode peut être déterminé avec une solution ferreuse en milieu tamponné par l'acide acétique et l'acétate, contenant du versénate. Après le point équivalent on obtient de nouveau un couple rédox rapide, savoir FeY^{-}/FeY^{-2}.

4.2. (b) Dosage du cyanure. La détermination iodométrique du cyanure, très ancienne[56] mais rarement citée[57], a été soumise à un examen plus approfondi. Il a été constaté que le pH doit être au moins 8. L'addition d'iodure est défavorable. La Fig. 14 fait voir quelques courbes de titrage.

4.3. Oxydation de l'iodure donnant l'iode unipositif

Les publications les plus connues sont celles d'ANDREWS[58] et de LANG[59].

Nous avons effectué les titrages avec trois réactifs différents: l'iodate, le periodate et le bromate. Nous avons observé aussi l'influence des acides chlorhydrique, bromhydrique et cyanhydrique. Dans le milieu chlorhydrique on distingue toujours deux stades de l'oxydation: le premier jusqu'à l'iode zérovalent, le deuxième jusqu'à l'iode unipositif. La netteté du premier point équivalent diminue à mesure qu'augmente la concentration en bromure. En présence de l'acide cyanhydrique l'oxydation donne toujours uniquement l'iode unipositif.

La vitesse de réaction la plus grande s'obtient en milieu cyanhydrique. En comparant les trois réactifs entre eux, nous constatons que le bromate réagit le plus promptement et le periodate le moins. Diverses courbes de titrage sont représentées dans les Figs. 15-18. En milieu acide cyanhydrique les courbes de titrage ressemblent à celle de la Fig. 4, quoi que ce soit le réactif employé; seulement la partie courbée n'est pas symétrique.

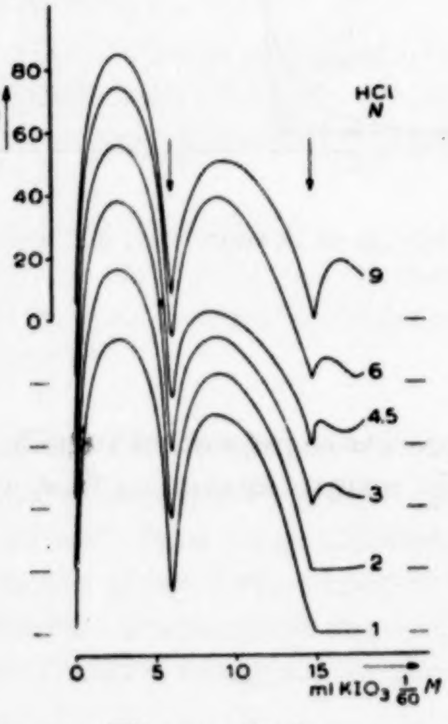

Fig. 15. Titrage d'iodure avec de l'iodate en milieu acide chlorhydrique.

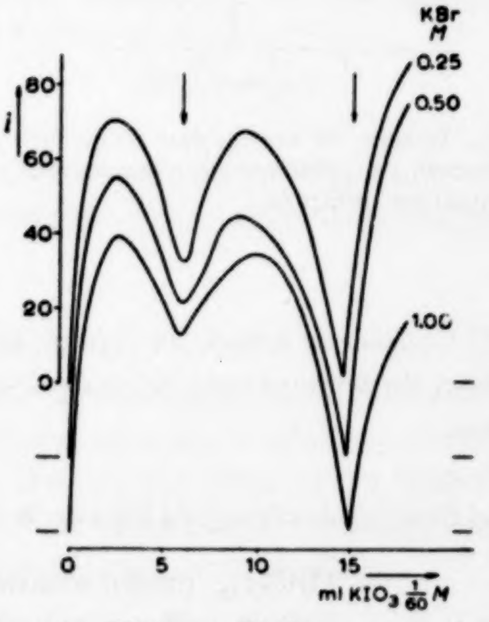

Fig. 16. Titrage d'iodure avec de l'iodate en milieu acide bromhydrique.

4.4. Complexes mercuriques

Comme nous l'avons déjà expliqué, on peut faire le titrage mercurimétrique du versénate par l'application de la méthode du „dead stop" si l'on munit le récipient de deux électrodes de mercure.

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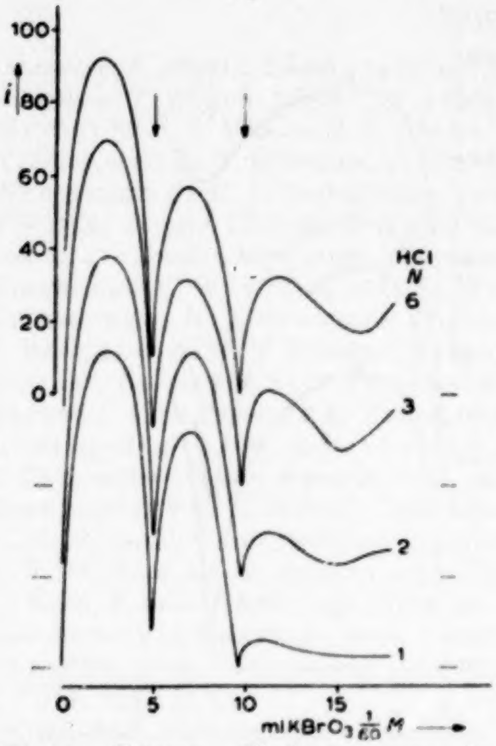

Fig. 17. Titrage d'iodure avec du bromate en milieu acide chlorhydrique.

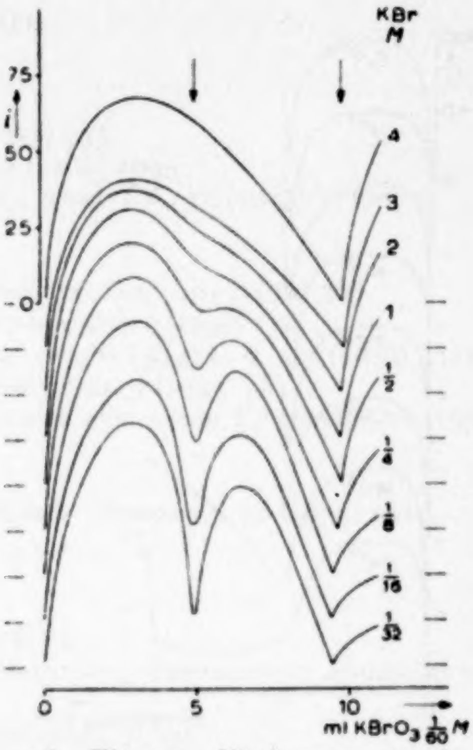

Fig. 18. Titrage d'iodure avec du bromate en milieu acide bromhydrique.

Mais il y a un très grand nombre d'autres cations formant des complexes avec le versénate. Nous avons constaté que beaucoup d'entre ceux-ci peuvent être déterminés indirectement. A cet effet on ajoute une quantité connue de versénate dont on mesure l'excès par titrage mercurimétrique. A l'encontre de mon attente, j'ai réussi à déterminer ainsi différents cations formant des complexes moins stables que l'ion mercurique. Ceci est en connexion avec la lenteur déjà signalée[60,61] de la dissociation de complexes chélatiques. On voit le comportement de plusieurs cations dans la Fig. 19.

La thiourée aussi est une substance donnant avec l'ion mercurique un complexe très stable en milieu faiblement acide[62]; il a la composition suivante: $\mathrm{Hg}\left(\mathrm{S}=\mathrm{C}\begin{matrix}\diagup \mathrm{NH_2} \\ \diagdown \mathrm{NH_2}\end{matrix}\right)_2^{+2}$.
La formule $\mathrm{Hg}\left(-\mathrm{S}-\mathrm{C}\begin{matrix}\diagup\!\!\diagup \mathrm{NH} \\ \diagdown \mathrm{NH_2}\end{matrix}\right)_2$, proposée par des auteurs tchèques[63] n'est pas exacte.
En effet, la N,N,N',N'-tétraméthylthiourée se fait déterminer de même manière. Outre le titrage de divers dérivés méthyliques, on réussit aussi à titrer l'allylthiourée et l'éthylènethiourée. La présence de chlorure nuit à la netteté avec laquelle se fait déterminer le point équivalent (Fig. 20).

On peut de la même manière titrer l'éthylènediamine et la cyclohexanediamine-1,2 et pourvu qu'on se serve, pour éviter leur décomposition, de chlorure mercurique, le thiosulphate et le thiosemicarbazide.

4.5. *Titrage direct de l'ion ferrique avec le versénate*

On peut réaliser ce dosage[64] en présence d'un tampon formique en opérant de préférence à une température un peu plus élevée (45°C), pourvu qu'on ajoute une petite quantité de l'ion ferreux et qu'on exclut l'air. Le courant avant le point équivalent est provoqué par le système Fe^{+3}/Fe^{+2} à peu près réversible; après le point équivalent par le couple FeY^{-}/FeY^{-2}, dont la réversibilité est meilleure.

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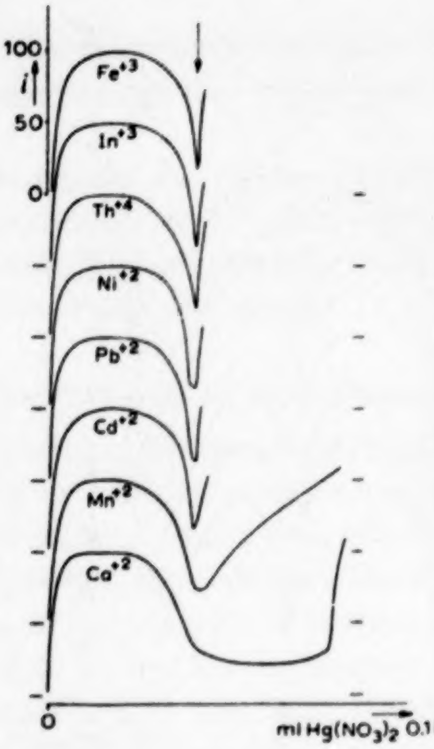

Fig. 19. Solution tamponnée de l'acétate et de l'acide acétique, contenante le cation indiqué et du versénate, dont l'excès est titré avec du nitrate mercurique.

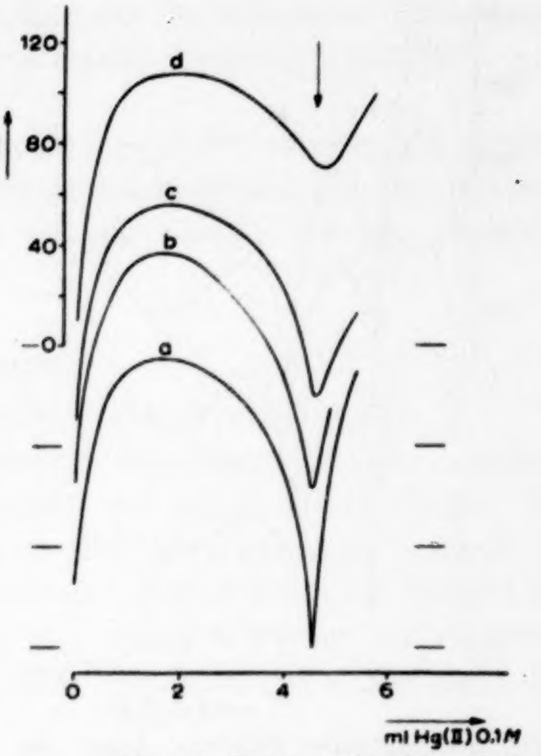

Fig. 20. Titrage de thiourée.

Sol. de base	*Sol. titrée*
a. 0.15M KNO_3; 0.1N HNO_3	$Hg(ClO_4)_2$
b. 0.15M KNO_3; 0.1N HNO_3	$HgCl_2$
c. 0.25M KNO_3	$HgCl_2$
d. 0.25M KCl	$HgCl_2$

4.6. Système Cu(II)/Cu(I)

En présence de solutions très concentrées de chlorure ou de bromure, ce système rédox se montre réversible. C'est ce qui rend possible la détermination chromométrique du cuivre divalent[65] selon la méthode du ,,dead stop''. Lorsqu'on ajoute à une solution de vanadate ou de dichromate[66] une quantité quelconque de cuivre divalent, le titrage de ces anions est devenu possible. Dépassé le point équivalent, l'ion chlorocuprate sera réduit, ce qui fait dévier le spot du galvanomètre.

CONCLUSION

Je ne puis mieux faire, pour terminer que de citer l'avis de **Delahay**[67] concernant la méthode du ,,dead stop''. L'introduction de cette méthode n'a pas élargi les possibilités de poursuivre les titrages par la voie électrométrique. Ce qui fait l'attrait de cette méthode, ce sont uniquement la simplicité du dispositif et la netteté avec laquelle on peut, même pour des concentrations très faibles[68] déterminer le point équivalent d'un titrage.

RÉSUMÉ

Les courbes de polarisation ont permis de prévoir divers cas d'utilisation de la méthode du "dead stop". Quelques exemples nouveaux sont donnés.

SUMMARY

Based on polarisation curves, one may forecast in various cases, the utility of the "dead stop" method. Several new examples are given.

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DISCUSSION

Dr. Ing. J. Tacussel (Lyon):
(1) Ordre de grandeur de la différence de potentiel appliquée entre les électrodes?
(2) Ordre de grandeur de courant?
(3) Peut-on opérer avec courant constant au lieu de tension constante?

Dr. H. L. Kies:
(1) Quelques millivolts.
(2) Microampère, dépendant de la concentration.
(3) Voir l'exposé du Dr. Gauguin.

Prof. G. Charlot (Paris):

Mais l'utilisation de differences de potentiel très variées et parfois très grandes entre les deux électrodes donne d'autres possibilités.

Dr. H. L. Kies:

Surtout quand la réversibilité des systèmes rédox impliqués n'est pas bonne, il est avantageux d'appliquer des tensions plus grandes. Parfois on peut tirer profit des parties parasitaires des courbes de polarisation.

Prof. D. Monnier (Genève):

Précision et sensibilité de cette méthode? Peut-on déterminer la constante de complexation et avec quelle précision?

Dr. H. L. Kies:

Précision dépendant de la concentration. Avec des liqueurs titrées 0.1*N*, ± 0.1%. On peut déterminer des solutions 0.0001*N*.

La constante d'un complexe mercurique se détermine polarographiquement ou potentiométriquement.

Prof. I. M. Kolthoff (Minneapolis):

Dr. Kies has illustrated in his lecture how many applications one can make of the same principles.

Question: In which respect does the amperometric titration method with two electrodes have advantages over the classical methods with one electrode? In my opinion there are hardly advantages.

Dr. H. L. Kies:

The advantages may be:
(1) The electrode system is more simple.
(2) It is not necessary to rule a polarogram in advance for knowing the tension to be applied.
(3) In dilute solutions, there is no need to fear that the concentration would be diminished by electrolysis (except systems as $NH_2OH + O_2$); so, it is possible to use larger electrodes which increase the current.
(4) Because of the resistance of solution and galvanometer, the curve becomes very acute near the end-point (*cf.* Fig. 13). Therefore, one can estimate the end-point accurately without plotting. A disadvantage would be the necessity of having one rapid redox system. However, when a Pt electrode is applied to redox titrations, I think the stability of the classical amperometric method becomes poor when both the redox systems are of the slow type.

Prof. P. Delahay (Baton Rouge):

In connection with Prof. Kolthoff's remark, it is worth noting that voltammetric titrations with two polarized electrodes are of interest because of the simplicity of the experimental set up. This is particularly so in titrations with non-aqueous solutions.

POTENTIOMÉTRIE À INTENSITÉ CONSTANTE

par

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La potentiométrie à intensité constante est une généralisation de la potentiométrie classique. Elle est décrite depuis trente ans[1,2] et malgré cela elle reste peu utilisée. Ceci est probablement dû à une mauvaise compréhension des phénomènes, pouvant provoquer l'emploi de mauvaises conditions opératoires et l'obtention de résultats erronés.

Dans ces dernières années, différents auteurs[3-7] ont établi les principes fondamentaux de la méthode et précisé les conditions opératoires exactes à utiliser.

FONCTIONNEMENT DE L'ÉLECTRODE INDICATRICE

Pour comprendre les phénomènes observés en potentiométrie à intensité constante, nous devons faire une courte incursion dans le domaine de l'électrolyse et plus particulièrement dans celui des courbes de polarisation.

En effet, si l'électrolyse peut être utilisée directement en analyse, pour réaliser quantitativement des réactions (dépôt d'un métal ou d'un oxyde sur une électrode, coulométrie) les phénomènes aux électrodes peuvent servir à déterminer des concentrations directement (polarographie) ou à suivre les variations de concentration au cours d'un dosage et déceler ainsi le point équivalent.

L'électrode est alors indicatrice d'une concentration et les phénomènes d'électrolyse ne doivent mettre en jeu qu'une quantité négligeable des corps dosés.

Courbes de polarisation

D'une façon plus précise, on peut dire que les méthodes électrochimiques de détection du point équivalent sont basées essentiellement sur les propriétés des courbes de polarisation.

En effet le plus souvent, les réactions d'oxydo-réduction ne peuvent être réalisées en un temps acceptable qu'irréversiblement. Les problèmes sont donc le plus souvent du domaine de la cinétique. Ils doivent donc être abordés au moyen des courbes de polarisation $I = \mathrm{f}(E)$.

Nous allons considérer le cas simple d'une réaction de précipitation d'un réducteur par un corps inerte aux électrodes:

$$\mathrm{Red} + A \rightarrow A\,\mathrm{Red}$$

La courbe de polarisation due à ce réducteur a une forme analogue à celle de la courbe de la Fig. 1. Au cours de la précipitation, la concentration de ce réducteur diminue, la hauteur de la vague diminue aussi et tend vers zéro.

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Si la réaction est suffisamment quantitative la hauteur de la vague s'annule pour une quantité de A très voisine de la quantité équivalente à celle de Red.

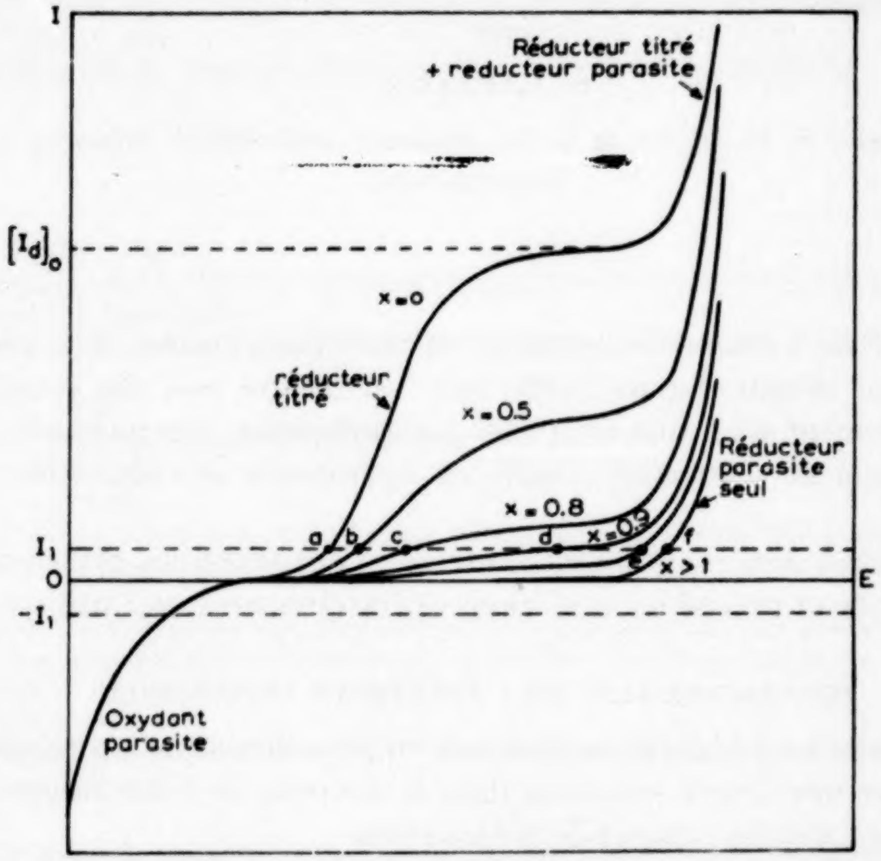

Fig. 1. Variation de la courbe de polarisation d'un réducteur au cours de sa précipitation.

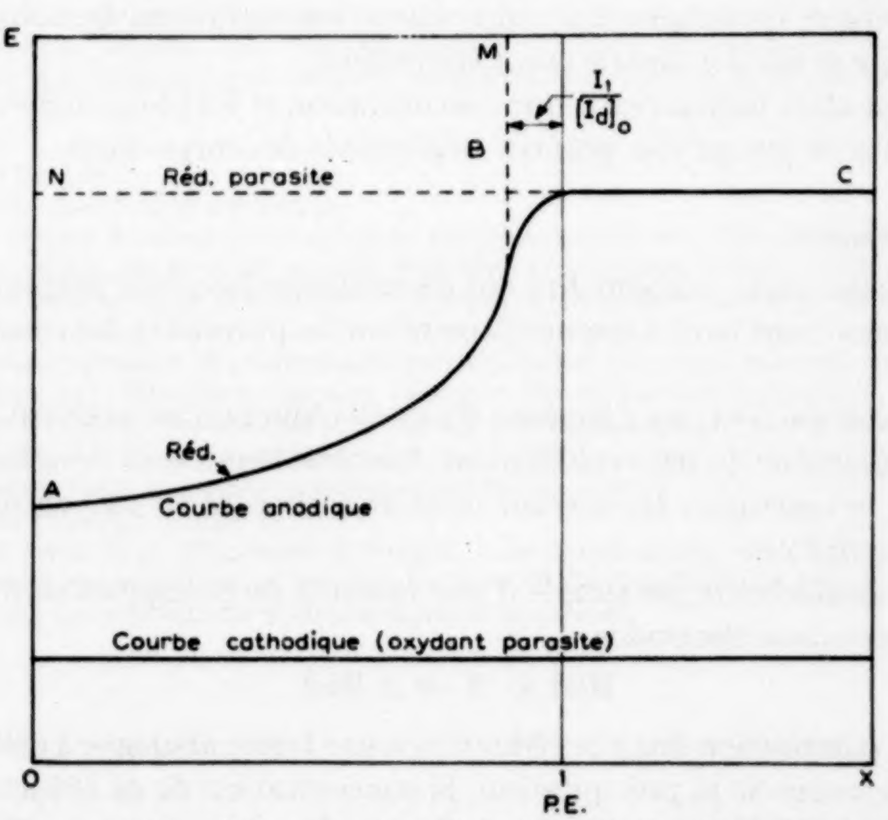

Fig. 2. Courbes potentiométriques au cours de la précipitation d'un réducteur électroactif.

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Supposons alors que par un moyen quelconque on maintienne l'intensité traversant la cellule constante au cours du dosage (mais suffisamment petite pour que la consommation de la substance à doser soit négligeable). Le potentiel de fonctionnement de l'anode, représenté par l'intersection des courbes avec la droite d'ordonnée égale à l'intensité imposée subit une variation brusque lorsque la valeur du courant limite est égale à l'intensité imposée.

On peut donc concevoir intuitivement que si l'intensité imposée est suffisamment petite, le saut de potentiel se produira pratiquement au point équivalent du dosage.

La courbe potentiométrique obtenue en mesurant le potentiel de cette électrode vis-à-vis d'une électrode de référence a une forme analogue à celle de la Fig. 2.

Conditions nécessaires à l'exactitude du dosage

Il est très difficile de résoudre quantitativement le problème dans sa généralité. Cependant, moyennant certaines hypothèses simplificatrices on peut apprécier l'importance des facteurs qui interviennent.

Les hypothèses qu'il est utile de faire sont les suivantes (dans le cas du dosage simple envisagé ci-dessus):

(1) La solution contient un excès d'électrolyte indifférent de telle sorte que le phénomène de migration n'agit pratiquement pas sur la courbe de polarisation. En chaque point, l'ordonnée est proportionnelle à la concentration.

(2) La réaction est rigoureusement quantitative de telle sorte que la concentration du composé Red diminue linéairement jusqu'au point équivalent en fonction de la quantité de solution titrante ajoutée. Autrement dit on peut écrire simplement

$$[\mathrm{Red}] = C_{\circ}\,(1-x)$$

où [Red] représente la concentration du réducteur, après avoir ajouté la fraction x de la quantité équivalente de A. $C_{\circ}$ est la concentration initiale.

(3) L'intensité imposée est suffisante et le système oxydo-réducteur auquel appartient Red suffisamment irréversible pour que le point de fonctionnement de l'électrode soit dans la zone d'irréversibilité de la courbe de polarisation (c'est-à-dire dans la zone où l'oxydant antagoniste éventuel n'agirait pas sur la forme de la courbe)[8]. Dans ces conditions l'équation de la courbe de polarisation est simplifiée:

$$E = E_{\circ} + \frac{RT}{\beta F} \log \frac{I}{I_d - I}$$

l'intensité limite de diffusion I_d étant donnée par la relation

$$I_d = k[\mathrm{Red}]$$

La combinaison de ces trois équations permet d'obtenir l'équation de la courbe potentiométrique avant le point équivalent

$$E = E_{\circ} + \frac{RT}{\beta F} \log \frac{I_1}{[I_d]_{\circ}} - \frac{RT}{\beta F} \log \left(1 - x - \frac{I_1}{[I_d]_{\circ}} \right)$$

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Dans cette équation $[Id]_0$ représente l'intensité de courant limite de diffusion dans les conditions initiales ($[Id]_0 = k\,C_0$) et I_1 l'intensité imposée.

On voit que l'on doit avoir une courbe logarithmique ayant une asymptote verticale correspondant au saut de potentiel pour une abscisse égale à $1 - \left[\frac{I_1}{Id}\right]_0$ (Fig. 2).

En réalité le potentiel ne monte pas à l'infini; la solution contient en général d'autres corps oxydables ne participant pas à la réaction ou le solvant lui-même peut s'oxyder. Le potentiel est donc limité après le point équivalent à une valeur E_B.

On peut alors calculer la valeur de l'abscisse du point B

$$x_B = \left(1 - \frac{I_1}{[Id]_0}\right)\left(1 - e^{\frac{-\beta F}{RT}(E_B - E_A)}\right)$$

On peut considérer que le saut de potentiel que l'on détectera se produira pour une valeur de x pratiquement égale à x_B. L'écart $\frac{I_1}{[Id]_0}$ représente la différence entre l'abscisse de l'asymptote verticale et celle du point équivalent.

Le terme $e^{\frac{-\beta F}{RT}(E_B - E_A)}$ représente l'écart supplémentaire qui peut se produire si la variation du potentiel est trop limitée par un réducteur parasite.

Pratiquement pour avoir un dosage précis à 0.2% près il faut que chacun de ces deux écarts soit en première approximation inférieur à 0.1 %. Autrement dit, l'intensité imposée devra être inférieure au millième de l'intensité limite initiale et l'écart entre les potentiels d'oxydation de réducteur à titrer et du réducteur parasite devra être pratiquement supérieur à 360 mV (en admettant $\beta = 1/2$ et un seul électron mis en jeu).

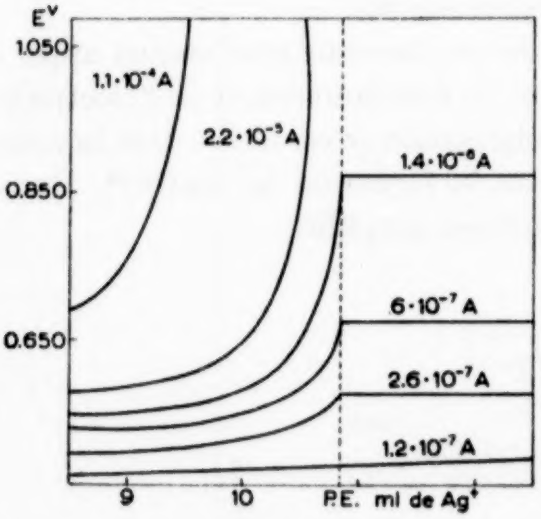

Fig. 3. Potentiométrie à intensité constante (précipitation de (SCN)Ag).

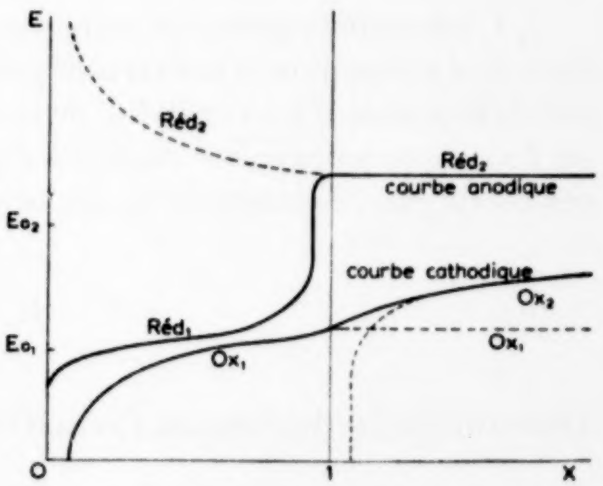

Fig. 4. Variation du potentiel de cathode et d'anode lors du dosage d'un réducteur „réversible" par un oxydant „irréversible".

Ceci est illustré par la Fig. 3 où sont tracées les courbes potentiométriques obtenues en suivant sur une anode de platine la concentration du thiocyanate au cours de la précipitation du thiocyanate d'argent. On voit l'importance de l'intensité du courant imposé.

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Influence des différents facteurs expérimentaux

L'augmentation de la surface de l'électrode pour une intensité imposée permet de diminuer le rapport $\frac{I}{[I_d]_0}$. Cela a peu d'utilité.

L'agitation de la solution ou de l'électrode agit de la même façon.

L'excès d'électrolyte indifférent dont nous avons admis l'existence pour simplifier les calculs n'est pas nécessaire. La courbe potentiométrique garde une forme analogue. D'ailleurs on peut concevoir que l'écart entre les deux courbes est d'autant plus petit qu'on est plus près du point équivalent puisque la concentration du corps titré diminue vis-à-vis des autres concentrations, et par suite son nombre de transport.

Lorsque la réaction employée est insuffisamment quantitative on peut montrer que la courbe prend l'allure d'une courbe potentiométrique habituelle avec le point équivalent au voisinage du point d'inflexion de la courbe.

GÉNÉRALISATION À TOUS LES TYPES DE DOSAGES

Ce que nous venons de dire pour le cas simple des dosages par précipitation est valable pour tous les types de dosages.

Les formes de courbes différentes peuvent cependant être obtenues par suite de l'existence de plusieurs systèmes oxydo-réducteurs participant à la réaction (cas des dosages par oxydation ou réduction). On peut prévoir — comme précédemment — une courbe anodique ou une courbe cathodique analogues à celles de la Fig. 4.

Les dosages par formation de complexe donnent des courbes analogues à celles obtenues pour la précipitation. La théorie des courbes est d'ailleurs identique si le complexe se dissocie lentement pour donner deux vagues successives sur la courbe de polarisation.

Les conditions d'exactitude sont toujours doubles:

(1) Dans tous les cas l'intensité imposée doit être petite vis-à-vis de l'intensité limité qui pourrait être obtenue initialement.

(2) Il y a toujours une condition de potentiel pour pouvoir observer le saut de potentiel du point équivalent.

POTENTIOMÉTRIE AVEC OU SANS ÉLECTRODE DE RÉFÉRENCE

Pour suivre un dosage par potentiométrie à intensité constante il suffit donc d'après ce que nous venons de voir, d'effectuer une électrolyse entre deux microélectrodes avec une intensité constante, convenablement choisie et de mesurer le potentiel d'une des électrodes par rapport à une électrode de référence classique.

En réalité ce schéma n'est jamais utilisé. On peut employer l'électrode de référence elle-même, comme électrode auxiliaire pour l'électrolyse. Le courant qui la traverse est suffisamment petit en général pour que son potentiel reste constant et bien défini.

On utilise ainsi une électrode de référence et une électrode indicatrice comme en potentiométrie classique.

Mais il existe un montage beaucoup plus avantageux. On peut supprimer l'électrode de référence et employer simplement deux électrodes indicatrices entre lesquelles on fait passer le courant constant.

La variation de la différence de potentiel entre les deux électrodes correspond à la différence des variations de potentiel de chacune des électrodes. Dans le cas d'une réaction de précipitation ou de formation de complexe la deuxième électrode métallique a généralement un potentiel sensiblement constant et la courbe potentiométrique reste analogue à celle de la Fig. 2.

Nous donnons à titre d'exemple la courbe potentiométrique obtenue en titrant le complexon par du cuivre en présence de thiocyanate (Fig. 5).

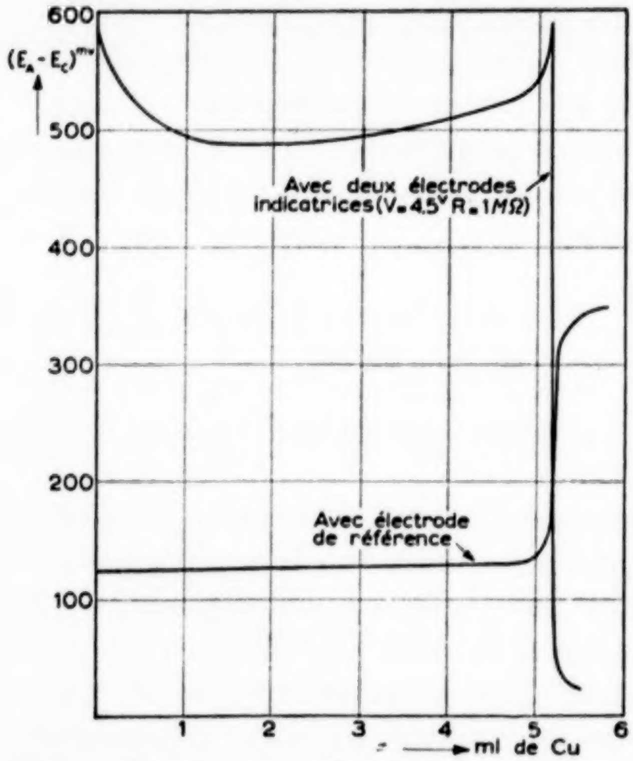

Fig. 5. Dosage potentiométrique du complexon par le cuivre en présence de thiocyanate.

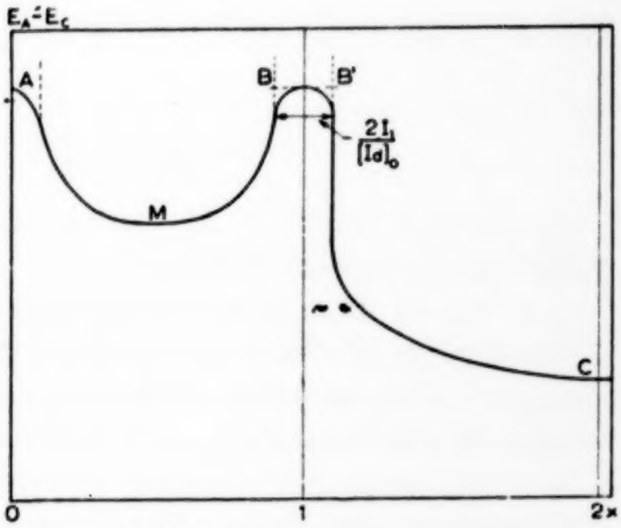

Fig. 6. Courbe potentiométrique obtenue au cours de l'oxydation d'un réducteur „irréversible" par un oxydant „irréversible" en utilisant deux électrodes indicatrices.

Dans le cas d'une réaction d'oxydo-réduction, le potentiel de chacune des électrodes varie brusquement au voisinage du point équivalent, l'une légèrement avant ce point et l'autre un peu après. La différence des potentiels passe par un maximum au point équivalent et permet ainsi de le déceler (Fig. 6).

Si le courant imposé est suffisamment petit ce maximum est aigu et son abscisse est repérable avec précision. Les conditions d'exactitude sont évidemment identiques à celles définies ci-dessus.

L'ordonnée de la courbe de chaque côté du point équivalent est une fonction de l'irréversibilité des systèmes redox mis en jeu et croît avec elle: plus le système auquel appartient le corps titré est réversible plus la différence de potentiel est faible avant le point équivalent et plus le système auquel appartient le corps titrant est réversible plus la différence de potentiel est faible après le point équivalent.

A titre d'exemple, nous représentons sur la Fig. 7 la courbe de dosage obtenue lors du titrage de Fe(II) par $Cr_2O_7^{-2}$ avec deux électrodes indicatrices.

MONTAGE ÉLECTRIQUE — CHOIX DES CONDITIONS OPÉRATOIRES

Conditions idéales

Considérons le montage électrique schématisé sur la Fig. 8. *V* est une tension variable à volonté, R une résistance (comprenant la résistance interne de la source V), r la résistance interne de la cellule d'électrolyse, v un voltmètre à grande résistance interne.

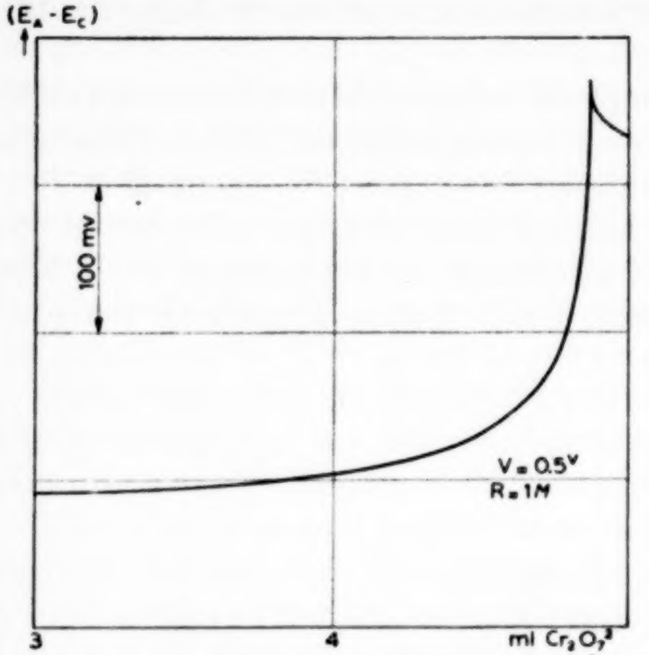

Fig. 7. Dosage de Fe(II) par $Cr_2O_7^{-2}$ potentiométrie avec deux électrodes de platine.

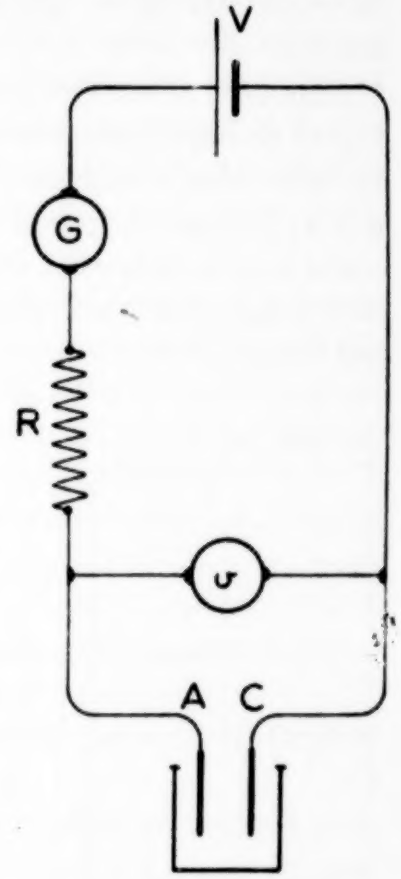

Fig. 8. Montage d'électrolyse.

G = galvanomètre
V = F-E-M réglable
A et C = électrodes
V = voltmètre électronique
R = résistance réglable

Soit I l'intensité traversant la cellule d'électrolyse, on peut écrire

$$I = \frac{V - E_A + E_C}{R + r}$$

si E_A et E_C sont les potentiels des deux électrodes.

Les deux équations des courbes de polarisation anodique et cathodique, couplées avec l'équation précédente permettent de calculer la variation de I ou de E au cours du dosage. C'est ce que nous avons fait dans le cas particulier où I est une constante.

Remarquons dès maintenant que pour une valeur donnée de V et $R + r$ les courbes $I = f(x)$ ou $E_A - E_C = f(x)$ seront analogues puisque I et $E_A - E_C$ sont des fonctions linéaires l'une de l'autre.

Pour réaliser une électrolyse à intensité constante on voit qu'il suffit de prendre une tension V et une résistance R suffisamment grandes. Dans ces conditions la variation relative de I est faible et il est plus facile de suivre la variation de $E_A - E_C$ au cours du dosage. Ceci, joint au fait que les courbes obtenues avec une électrode de référence sont très voisines des courbes potentiométriques — nous a fait dénommer cette méthode, potentiométrie à intensité constante.

C'est avec ces conditions opératoires qu'ont été obtenues les courbes des Figs. 3 et 5. Pour la courbe de la Fig. 5, la tension extérieure était simplement fournie par une pile ordinaire de 4.5 V et la résistance en série était une résistance radio, soudée entre un des pôles de la pile et la prise de courant. La différence de potentiel $E_A - E_C$ était mesurée avec un pH-mètre comportant une graduation en mV (celle-ci n'étant d'ailleurs pas nécessaire).

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Réalisation approximative des conditions théoriques

En fait, on peut concevoir à partir de la forme des courbes de polarisation — et l'expérience le vérifie — que les conditions expérimentales peuvent varier dans certaines limites.

Ainsi nous avons indiqué sur la Fig. 9 des exemples de variation de la différence de potentiel et de l'intensité pour différentes valeurs de la tension appliquée et de la résistance en série. Une variation d'intensité dans un rapport de 50 (pour $R = 5 \cdot 10^4\ \Omega$ et $V = 0.5$ V) n'empêche pas d'avoir une courbe d'allure potentiométrique avec encore une variation de potentiel assez brutale au point équivalent. En augmentant V à 2 V et R à 1 MΩ, I ne varie plus que dans un rapport de 1 à 1.5 et la variation de potentiel est très brutale.

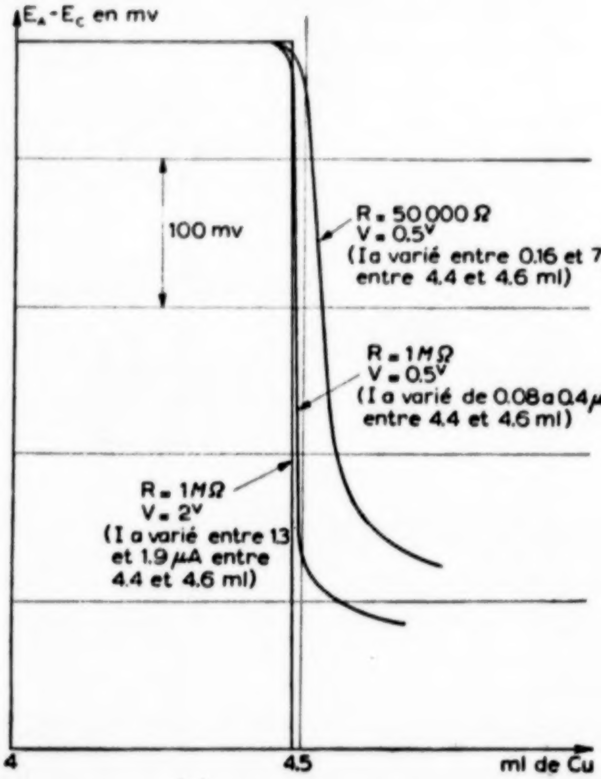

Fig. 9. Dosage du complexon par le cuivre. Montage avec deux électrodes de platine.

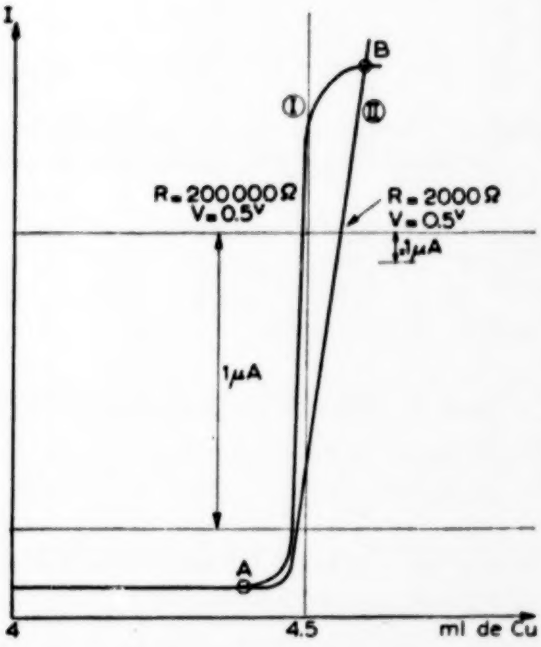

Fig. 10. Dosage du complexon par le cuivre. Montage avec deux électrodes de platine. Courbe tracée en prenant *A* et *B* communs.

Dans le cas où R n'est pas trop grand évidemment la mesure de I comme celle de $E_A—E_C$ sont également utilisables (Fig. 10, courbe I). On voit sur ces exemples, que même lorsque le courant reste suffisamment faible pour que la condition imposée par la précision reste vérifiée, si R est trop faible le point équivalent semble moins bien défini. Le saut de potentiel est plus progressif.

En effet si l'on diminue davantage R on arrive progressivement aux courbes ampérométriques[9]. Les caractéristiques sont maintenant inversées : les variations relatives de $E_A—E_C$ sont faibles ($E_A—E_C \neq V$) alors que les variations de I sont importantes et on mesure donc plutôt l'intensité.

Alors que sur la courbe I ou $E_A—E_C$ en potentiométrie le point équivalent est marqué par une partie verticale, sur les courbes ampérométriques il est marqué par un changement de pente. Cette distinction est importante: même si la forme des courbes

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est souvent apparemment le même — en particulier pour l'ampérométrie avec deux électrodes indicatrices, généralisation de la méthode du „dead-stop end point", et pour la potentiométrie à intensité constante avec deux électrodes indicatrices — la détection du point équivalent exige une mesure plus exacte sur la courbe ampérométrique que sur la courbe potentiométrique. Ceci est visible sur la Fig. 10 où nous avons représenté les courbes d'intensité obtenues — toujours dans le dosage du complexon par le cuivre — avec $R = 2{,}000\ \Omega$ et $R = 200{,}000\ \Omega$ pour une tension appliquée de 0.5 V (les échelles d'intensité ont été choisies pour que les points à 0.1 ml part et d'autre du point équivalent soient communs aux deux courbes).

Le même phénomène apparaît déjà (Fig. 9) sur la courbe de variation de la différence de potentiel avec $R = 50{,}000\ \Omega$ (comparée à la courbe obtenue avec $R = 1\ \mathrm{M}\Omega$).

Cette observation est importante pour la construction des appareils automatiques: l'arrêt du dosage à une différence de potentiel donnée donnera un résultat d'autant plus précis que les conditions de la potentiométrie seront mieux respectées.

Si les conditions sont trop voisines de celles de l'ampérométrie, le seuil de déclenchement doit être choisi tout au début de la variation de $E_A—E_C$ (ou de I) et ceci peut provoquer des difficultés (s'il y a une légère instabilité du potentiel par exemple à l'addition de la solution titrante, si la réaction n'est pas rigoureusement quantitative, etc., tout ceci ayant plus ou moins de répercussion selon le sens du dosage).

Au contraire, avec les conditions de la potentiométrie le choix du seuil de déclenchement a peu de répercussion sur la précision du dosage.

Si R est grand et V suffisamment petit, c'est-à-dire si I est très petit, on tend progressivement vers la potentiométrie classique, avec des sauts de potentiel plus faibles. Ici encore, pour l'emploi des titrimètres automatiques le choix du seuil reprend plus d'importance pour la précision.

Pratiquement il est convenable de choisir $V > 2\ V$ et $R >> 200{,}000\ \Omega$ en ajustant leur valeur pour que les conditions de précision définies précédemment soient vérifiées.

AVANTAGES DE LA MÉTHODE

La potentiométrie à intensité constante — ou approximativement constante — a l'avantage de permettre l'emploi des méthodes potentiométriques de détection du point équivalent, même avec des corps peu électroactifs. Des composés qui ne donnent pas de potentiel en potentiométrie classique peuvent cependant être dosés selon les méthodes potentiométriques avec ce procédé. Même avec les corps électroactifs les variations des grandeurs mesurées I ou $E_A — E_C$ sont plus importantes et la détection du point équivalent s'en trouve facilité.

Enfin, on peut éliminer l'électrode de référence. Ceci facilite beaucoup les manipulations et permet d'avoir une bonne précision sans prendre les précautions qui sont souvent nécessaires avec les électrodes de référence usuelles.

Un autre avantage de la méthode est qu'elle permet facilement de rendre le dosage automatique. La variation de la différence de potentiel aux bornes de la cellule ou celle équivalente de la chute ohmique proportionnelle à l'intensité d'électrolyse peuvent être utilisées pour provoquer l'arrêt d'une burette pour une valeur convenablement choisie de la grandeur mesurée.

Nous employons ainsi systématiquement pour différents dosages en série, des appareils construits à notre Centre de Recherches. La grandeur pilote est la chute ohmique aux extrémités de la résistance *R*. Elle commande, pour une valeur prédéterminée, un contacteur placé sur le circuit de la vanne électro-magnétique de la burette. Les électrodes sont deux fils de platine de 5 mm de long, 0.2 mm de diamètre. L'appareil permet de fixer à volonté *R* entre $5 \cdot 10^3$ et $2 \cdot 10^6$ Ω et *V* entre 0.5 et 2 V. On utilise en général une tension de 2 V et une résistance moyenne de 200,000 à 1 MΩ.

Les dosages peuvent ainsi être effectués avec une précision de 0.5% moyennant certaines précautions concernant l'agitation et la vitesse d'addition de la solution titrante.

Pour la mise au point de ces dosages on ne saurait d'ailleurs trop recommander de déterminer expérimentalement au préalable les valeurs optima de *R* et de *V* en traçant les courbes de dosage.

Vis-à-vis de l'ampérométrie on peut dire que pour un dosage manuel, les deux méthodes sont équivalentes, bien que l'expérience montre parfois une meilleure précision en ampérométrie. Avec un titrimètre automatique comme nous l'avons dit, la potentiométrie est préférable pour la plus grande latitude de réglage.

RÉSUMÉ

La potentiométrie à intensité constante est une généralisation de la potentiométrie classique. L'étude des variations de la courbe de polarisation de la solution à doser, au cours de l'addition de la solution titrante, permet de prévoir l'allure générale des courbes potentiométriques et les conditions expérimentales à réaliser pour détecter le point équivalent avec une précision suffisante.

Cette étude est faite quantitativement dans un cas simple d'une réaction de précipitation. Les résultats sont applicables — au moins qualitativement — aux autres types de réactions.

L'influence des conditions opératoires est montrée sur l'exemple du dosage du complexon par le cuivre en présence de thiocyanate. En particulier, on montre l'importance de la résistance du circuit d'électrolyse sur la forme de la courbe de dosage, celle-ci pouvant passer progressivement de la courbe potentiométrique à la courbe ampérométrique.

Les répercussions de cette déformation sur la détection du point équivalent, sont mises en évidence, en particulier dans le cas de l'emploi de titrimètres automatiques.

SUMMARY

Potentiometry at constant intensity is a generalization of classical potentiometry. A study of variations of the polarization curve of the solution to be analysed, during the addition of the titrating solution, allows one to forecast the general shape of the potentiometric curves and the experimental conditions necessary for detection of the equivalence point with sufficient precision.

This study has been made quantitatively in a simple case of a precipitation reaction. The results are applicable — at least qualitatively — to other types of reactions.

The influence of the operative conditions is shown by the example of the determination of complexon by copper in the presence of thiocyanate. In particular, the importance of the electrolysis circuit resistance is shown for the shape of the determination curve, this being able to pass progressively from the potentiometric curve into the amperometric curve.

The repercussions of this deformation for the detection of the equivalence point are demonstrated, particularly when using automatic titrimeters.

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DISCUSSION

Prof. J. E. DUBOIS (Paris et Sarrebruck):

Nous avons trouvé dès 1953 que les différences de potentiel entre électrodes de platine au cours d'un titrage peuvent être utilisées avec la „méthode potentiométrique à intensité variable".

Du point de vue instrumental il y a de grosses difficultés pour monter un titrimètre automatique basé sur le passage par une valeur fixe absolue de la différence de potentiel. En effet les potentiels aux électrodes et donc leurs différences ne sont pas reproductibles et peuvent varier de 10% environ. Dans ces conditions on peut difficilement utiliser un repère absolu de potentiel lorsque le saut de titrage est faible, par exemple de l'ordre de 60 mV dans certains dosages par complexométrie.

Nous croyons préférable de mesurer la différence de potentiel aux électrodes à l'aide d'un voltmètre électronique différentiel qui permet la mesure de la différence de potentiel par raport à un potentiel de référence, celui qui existe aux bornes des électrodes au début de l'analyse. On a réalisé ainsi un titrimètre très simple pour tous les dosages indiqués ici.

En outre si la tension E aux électrodes après la chute de tension dans le circuit d'électrolyse est de l'ordre de 2 V on peut titrer dans certains cas les acides et les bases (*Ann. Univ. Sarre*, 1953-54).

Je désirerais en outre faire remarquer que dans le domaine de l'instrumentation automatique on peut tirer parti des faux „end points" pour approcher mécaniquement du dosage par burette effectué à la main. (J. E. DUBOIS, *Conf. sur la Polarovoltrie*; M. GAUTIER, *Méthodes d'Analyse*, Masson et Cie, Paris, 1957).

Dr. R. GAUGUIN:

(1) Je ne crois pas à l'utilisation pratique de sauts de potentiel aussi faibles. Ou bien ils sont explicables selon les principes que j'ai rappelés, et dans ces conditions on peut agir sur l'intensité imposée pour augmenter le saut de potentiel si l'écartement des courbes de polarisation le permet ($E_B - E_A > 0.36$ V environ). Si cette condition n'est pas vérifiée le dosage risque d'être erroné. Ou bien ce sont des sauts de potentiel très faibles que l'on peut observer en titrant n'importe quel corps par n'importe quoi. Dans ce cas les phénomènes n'ont pas une signification simple, et dépendent toujours énormément des conditions opératoires (présence d'ions étrangers, agitation, etc.). Ils ne peuvent être utilisés avec sécurité pour des dosages. Aucune astuce électronique ne peut améliorer ceci.

(2) En ce qui concerne le dosage acide-base, je crois q'un titrimètre automatique avec deux électrodes de platine a peu d'utilité. Pour de tels dosages, on est en général très exigeant. On veut pouvoir distinguer entre différents acides (ou bases) de pK différents en s'arrêtant à un pH défini. Ceci est impossible avec un titrimètre automatique avec deux électrodes de platine. Je crois qu'il faut revenir dans ce cas au titrimètre avec électrode de verre.

Prof. I. M. KOLTHOFF (Minneapolis):

Dean DUBOIS has made an interesting application of potentiometric titrations at constant current. It does not work, however, in solutions which are not unbuffered at the end point.

COURBES INTENSITÉ-POTENTIEL DANS LES ÉCHANGEURS D'IONS

par

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L'électrochimie des résines échangeuses d'ions peut arbitrairement être divisée en deux sections: d'une part l'étude des phénomènes lorsque la résine est en contact avec des solutions ioniques, tel le cas des membranes, et d'autre part l'électrochimie dans les résines, c'est-à-dire lorsque celles-ci servent en quelque sorte de solvant. Dans ce cas seuls les cations peuvent exister en tant qu'ions mobiles dans le cas d'une résine échangeuse de cations.

Les études ont surtout porté sur la détermination des conductances des ions (voir par exemple bibl. 1), le calcul des coefficients de diffusion à l'aide desconduct ances équivalentes[2] et la migration des ions dans les résines[1,3] avec comme application les séparations par électromigration[4-6]. Peu d'auteurs[7,8] se sont intéressés aux phénomènes aux électrodes.

Nous nous sommes proposé d'aborder ces phénomènes et de voir, en particulier, s'il était possible de tracer des courbes intensité-potentiel comme dans le cas des solutions aqueuses.

Afin d'éviter les corrections de chute ohmique, on utilise généralement trois électrodes, l'une d'elles étant une électrode de référence par rapport à laquelle on détermine le potentiel imposé à l'électrode indicatrice. Nous avons donc d'abord été amenés à rechercher d'une part un système rédox rapide utilisable comme électrode de référence et d'autre part à déterminer la résistance de la cellule, afin d'effectuer la correction de chute ohmique, le montage à 3 électrodes nous étant apparu comme difficilement réalisable.

CONDITIONS OPÉRATOIRES

Préparation de la résine

Environ 5 g de résine (Dowex 50, X-12, 50 mesh) sont introduits dans un tube effilé à la partie inférieure. On fait couler une solution contenant le ou les cations que l'on désire fixer jusqu'à ce qu'ils apparaissent dans l'effluent. La résine est ensuite lavée à l'eau distillée jusqu'à disparition du cation ou de l'anion dans la solution. La résine est ensuite séchée à l'aide de papier filtre jusqu'à ce qu'elle n'adhère plus à celui-ci.

Cellule d'électrolyse

Elle est constituée par un tube de verre de 65 mm de longueur et de 14 mm de diamètre. La résine est tassée dans le tube à l'aide d'une baguette de verre et y est maintenu au moyen des deux électrodes mises en bout du tube.

Mesures conductimétriques

Les deux électrodes sont constituées par deux couvercles de creusets de platine. Les mesures sont effectuées à l'aide d'un conductimètre Philips GM 4249.

Tracé des courbes intensité-potentiel

La cellule est reliée à une source de tension continue par l'intermédiaire d'un galvanomètre SEFRAM type Lumindex. La différence de potentiel entre les électrodes est déterminée à l'aide d'un potentio-pH-mètre Tacussel.

RÉSULTATS EXPÉRIMENTAUX

(1) Résistance de la cellule

Mesures conductimétriques. Les résultats sont rassemblés dans le Tableau I. Les valeurs indiquées sont reproductibles à ± 5% près. Comme cela avait déjà été constaté[1] la résistance varie avec la fréquence du courant.

TABLEAU I

Résine	*Résistance (Ω)*	
	1000 c/s	*50 c/s*
H^+	250	
Cu^{+2}	4000	4600
Zn^{+2}	3900	
Ag^+	3550	3900

Électrolyse d'une résine Ag^+ (ou Cu^{+2}) entre électrodes d'argent (ou de cuivre). Les points expérimentaux représentatifs du courant d'électrolyse en fonction de la tension mesurée entre les électrodes s'alignent sur une droite (Fig. 1). On peut donc en conclure que, d'une part les systèmes Cu/Cu^{+2} et Ag/Ag^+ sont rapides, et que d'autre part la loi d'Ohm est suivie.

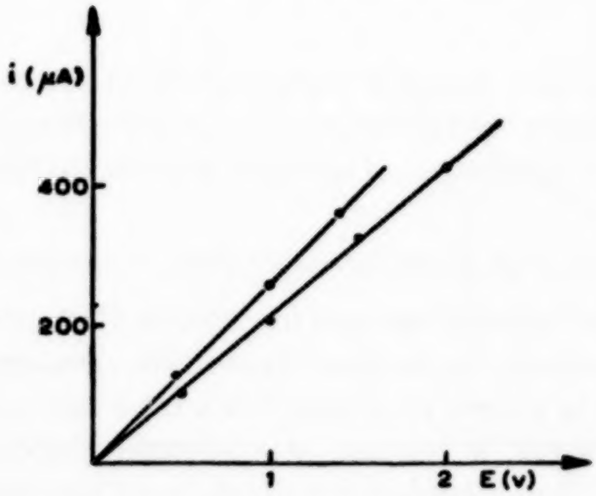

Fig. 1.

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La pente des droites représentée Fig. 1 est égale à l'inverse de la résistance de la cellule. Les résistances déterminées de cette façon sont égales à Ag^+ 4000 Ω et Cu^{+2} 4600 Ω. Ces valeurs sont en accord avec celles déterminées conductimétriquement en utilisant un courant de fréquence égale à 50 c/s.

(2) Choix d'une électrode de référence

Nous avons adopté le système Cu/Cu^{+2} comme système de référence. La résistance de la cellule variant de façon importante lorsque la nature de l'ion change, afin de ne pas être obligé de la déterminer dans chaque cas, la cellule est constituée de la façon suivante: elle est remplie sur 60 mm de résine sous forme Cu^{+2} et le reste est rempli sous la forme choisie. De la sorte avec une bonne approximation la résistance de la cellule est constante et égale à 4600 Ω.

(3) Courbes des différents systèmes

Les tensions lues au potentiomètre sont corrigées de la chute ohmique. Les résultats obtenus pour les différents systèmes sont rassemblés sur le Tableau II, les courbes correspondantes sont rassemblées Fig. 2.

TABLEAU II

Électrode	*Électrolyte*	*Réaction à l'électrode*	*Potentiel d'équilibre*	*Potentiel $i = 10\ A/cm^2$*
Cu	Cu^{+2}	$Cu^{+2} + 2e \rightleftarrows Cu$	origine	
Ag	Ag^+	$Ag^+ + e \rightleftarrows Ag$	+0.41 V	
Pt	H^+ Na^+	$2H_2O + 2e \rightleftarrows H_2 + 2HO^-$		— 0.35 V
Pt	H^+ Na^+	$2H_2O - 4e \rightleftarrows O_2 + 4H^+$		+ 1.45 V

Les courants anodiques sont comptés positivement et les courants correspondant à une réduction sont comptés négativement. Les potentiels correspondant à des systèmes plus oxydants que le système Cu/Cu^{+2} sont affectés du signe(+).

(4) Électrolyse en présence d'un électrolyte indifférent. Courant de diffusion d'un ion

Au cours des essais précédents, un seul ion mobile était présent dans la résine et il participait seul au transport du courant dans cette dernière. Par contre s'il existe deux ions mobiles dans la résine, et si l'un d'eux est à une concentration très grande vis-à-vis de celle du second, le courant sera presque exclusivement transporté par l'ion concentré. Mais si l'ion à faible concentration est susceptible de réagir au potentiel imposé à l'électrode, il se déplacera vers celle-ci par diffusion. Lorsque sa concentration à l'électrode sera nulle, la courbe intensité-potentiel correspondante présentera un palier de diffusion dont la hauteur sera proportionnelle à la concentration de l'ion.

Les essais ont été effectués avec les ions H^+ et Ag^+. La résine est préparée par passage d'une solution d'acide nitrique et de nitrate d'argent en proportions connues. Pour connaître le rapport Ag^+/H^+ dans la résine en fonction de ce même rapport en solution aqueuse, il faut connaître la constante de la loi d'action de masses correspondant à l'équilibre de ces deux ions entre les deux phases. Cette constante a été déterminée par analyse frontale[9,10] et a pour valeur numérique 3.5 ± 0.5.

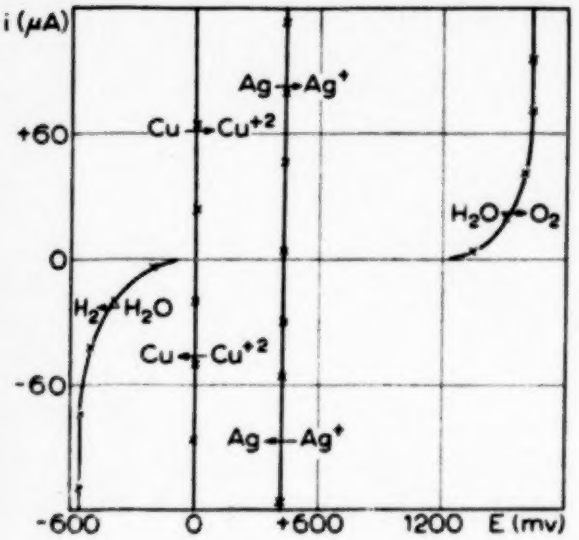

Fig. 2.

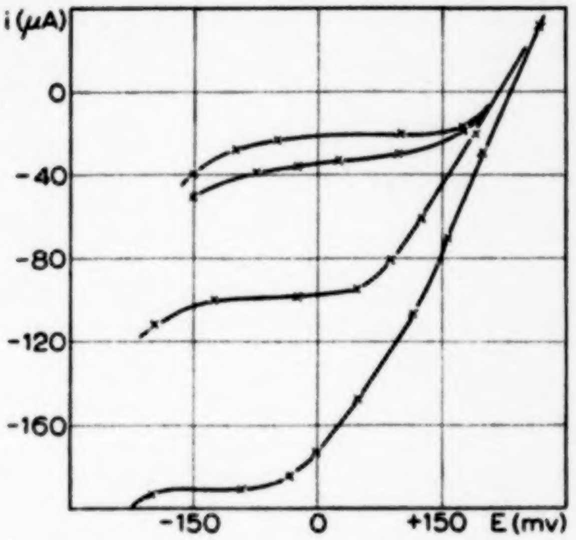

Fig. 3.

Le rapport Ag^+/H^+ en solution aqueuse est au maximum égal à $8.5 \cdot 10^{-3}$: donc dans la résine il ne dépasse pas $3 \cdot 10^{-2}$. Etant données les valeurs numériques de Tableau I, le nombre de transport des ions Ag^+ est toujours inférieur à $2 \cdot 10^{-3}$. La concentration de Ag^+ dans la résine est sensiblement proportionnelle au rapport Ag^+/H^+ dans la résine, car la concentration des ions H^+ est pratiquement constante et égale à la capacité de la résine. En définitive la concentration des ions Ag^+ dans la résine est proportionnelle au rapport Ag^+/H^+ dans la solution aqueuse ayant servi à préparer la résine. Les courbes intensité-potentiel correspondant à différentes valeurs de ce rapport sont représentées Fig. 3. La proportionnalité entre le courant de diffusion et la concentration de Ag^+ (ou du rapport Ag^+/H^+) est bien vérifiée (Fig. 4).

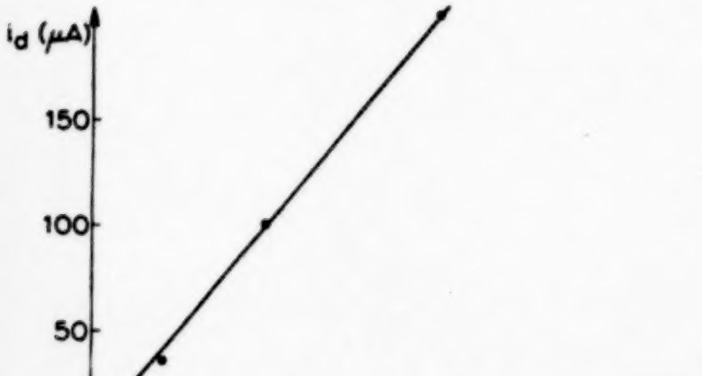

Fig. 4.

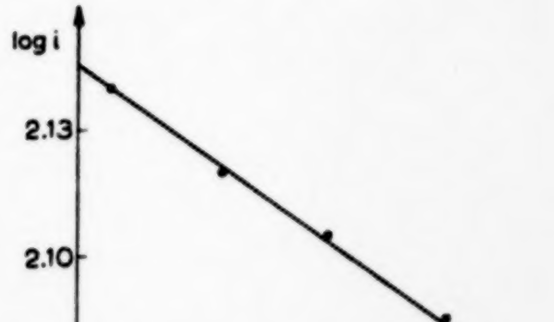

Fig. 5.

(5) Variation du courant en fonction du temps à potentiel constant

Si on impose à l'électrode d'argent un potentiel de —100 mV, les ions Ag^+ sont réduits. La concentration de ces derniers diminue dans la résine et il en est de même pour l'intensité du courant. La variation du logarithme de l'intensité en fonction du temps est représentée Fig. 5 dans le cas d'une résine préparée avec une solution aqueuse dont le rapport Ag^+/H^+ est égal à $8.5 \cdot 10^{-3}$. Le courant varie donc exponentionnellement en fonction du temps comme dans le cas des solutions.

En résumé, les phénomènes électrochimiques dans les résines échangeuses d'ions peuvent être interprétés comme dans le cas des solutions aqueuses.

RÉSUMÉ

Il est possible de tracer les courbes intensité–potentiel dans les résines échangeuses d'ions. Les phénomènes sont analogues à ceux observés en solution aqueuse.

SUMMARY

It is possible to plot intensity–potential curves in ion-exchange resins. The phenomena are analogous to those observed in aqueous solution.

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DISCUSSION

Prof. P. Delahay (Baton Rouge):

Comment mesurez-vous les courbes intensité–potentiel?

Dr. J. Coursier:

On impose la différence de potentiel entre les deux électrodes et on mesure l'intensité du courant traversant la cellule.

Prof. W. Kemula (Varsovie):

Avez-vous réussi à tracer des courbes d'autres ions outre Cu^{+2} et Ag^+?

Dr. J. Coursier:

Oui, nous avons pu tracer des courbes relatives aux systèmes Cd/Cd^{+2} et Fe^{+2}/Fe^{+3}, mais les résultats ne sont pas suffisamment confirmés pour pouvoir être communiqués.

COULOMETRIC DETERMINATIONS

by

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Coulometry applies Faraday's law to analytical chemistry. The experimental conditions must, therefore, be so chosen that a perfectly reproducible stoichiometric relation will exist between the amount of electricity and the constituents of the chemical reaction, on which the analytical method is based.

The original coulometric method, introduced by SZEBELLÉDY AND SOMOGYI[1], precisely measures the interval during which the electrochemical reaction, carried out with a constant current, takes place. It is known, however, that the potential of the electrode that liberates the active substance changes during the determination, owing to the fact that the composition of the solution changes during the electrolysis. This especially holds true at the end-point of the titration. Thus, for coulometric determinations under constant current, only those reactions are of importance for which it is possible to modify the experimental conditions so that the current under which the electrolysis is carried out is also of practically constant intensity.

A series of lead storage batteries can serve for getting a current of constant strength. SEASE, NIEMANN AND SWIFT[2] recommend the use of a dry cell battery with a higher voltage and resistance. A current of constant intensity can also be withdrawn from a potentiostat, or electronic control of the current strength can be used. Several authors have suggested instruments for direct use in coulometric determinations. LINGANE'S device maintains the current constant up to 0.01%. DEFORD and co-workers[3] proposed a motor generator with an output of 250 mA at 300 V. This equipment can guarantee a constant generation current within ± 0.1%.

The current intensity must be measured by a calibrated milliammeter. It is, of course, better to measure potentiometrically the decrease of e.m.f. of the battery discharged through a resistance of known value connected in parallel to the electrodes in the titration vessel.

We usually measure the time with a stop watch or a timer of the synchronous motor type. With electric timers, every change of frequency in the supply line results in an error of measurements. Stop watches working with a precision of ± 0.01 sec and a capacity of 100 sec are available.

SZEBELLÉDY[1] originally determined the end-point by means of an acid - base indicator.

A more complete utilization of the coulometric method was attained by introducing physico-chemical methods for indication. The amperometric indication (SEASE, NIEMANN, SWIFT[2]) is based on the use of two electrodes, one of which has a constant potential as a result of a constant concentration of one of the ions; the second indicator electrode changes its potential, either according to the concentration of the electrochemically active substance to be titrated, or according to the concentration of the active substance of the titration solution. The voltage used for polarizing the indicator electrodes must not decompose the supporting electrolyte. It must, however, be equal to the decomposition voltage of the supporting electrolyte with dissolved active substance or be higher (Fig. 1).

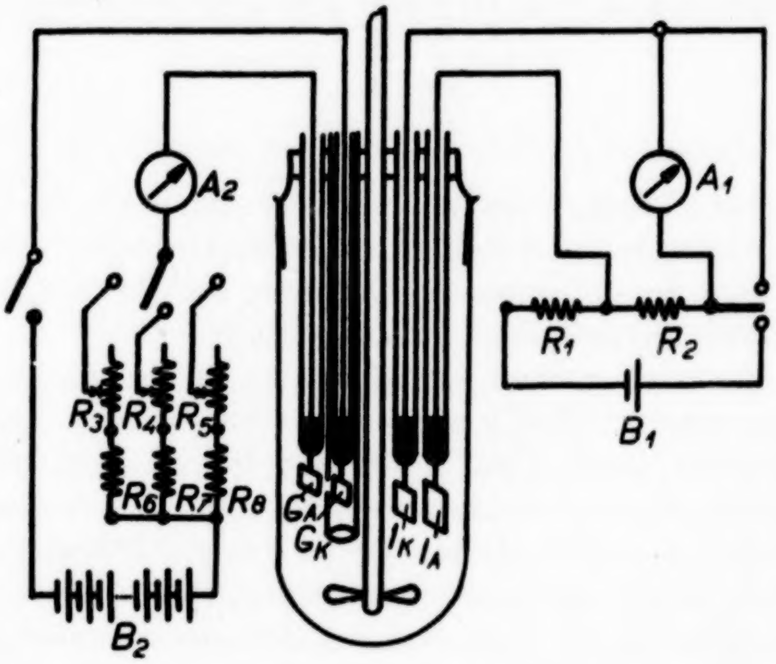

Fig. 1. Titration set according to MYERS AND SWIFT[4].
G_A, G_K = generator electrodes; I_A, I_K = indicator electrodes; B_1 = lead storage cell; B_2 = lead storage battery; R_1 . . . . . R_8 = regulating resistances; A_1 = microammeter; A_2 = milliammeter.

The indicator electrodes should be placed outside the electric field of the generation electrodes so as to avoid contact with the higher concentrations of the liberated titration substance. If this is not done, the end of the titration does not occur at the equivalence point.

The sensitivity of the indicator electrodes to an excess of the titration reagent liberated by the current depends on their treatment before titration. Sometimes generation of chlorine on their surfaces is useful.

LINGANE[5] recommends the use of only one indicator electrode, which is then connected with an electrolytic bridge to a calomel reference electrode placed outside the titration solution. CARSON[6] proposed a similar arrangement for titration with bromine.

The use of coulometric titration with potentiometric indication admits of the possibility to interrupt the titration precisely at the equivalence point (Fig. 2). EPSTEIN, SOBER AND SILVER[9] first used potentiometric indications in the titration of acids. Quinhydrone electrodes were used both for indication and reference electrodes.

COOKE, REILLEY AND FURMAN[10] proposed an arrangement employing equivalence point potential. A permanently polarized indicator electrode improves the results. The use of conventional photometric end-point detection methods prevents the formation of bubbles in the solution to be titrated. In spite of this, WISE and co-workers[11] suggest a differential system. FRANKLIN AND ROTH[12] measured the change in absorbancy of the solution to be titrated, which is caused by some suitable coloured substance produced or consumed at an electrode of the coulometric system.

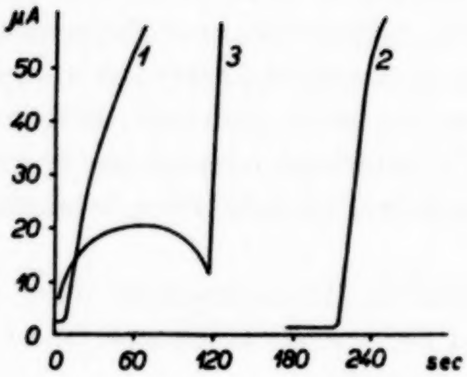

Fig. 2. Titration curves of some coulometric determinations with constant current[7,8].
1. Titration of 25 ml of 80% acetic acid containing 4% hydrochloric acid by means of chlorine (blank for the titration of erucic acid; 7.5 sec).
2. Titration of 25 ml of $2.16 \cdot 10^{-4}M$ solution (1836 mg) of erucic acid in 80% acetic acid, containing 4% hydrochloric acid, by means of chlorine (216.0 — 7.5 = 208.5 sec; 5 mA).
3. Titration of 25 ml of $1.2 \cdot 10^{-3}M$ solution (0.330 mg) of hydroquinone in $0.1 M$ HBr aqueous solution by means of bromine (116.0 sec, 5 mA).

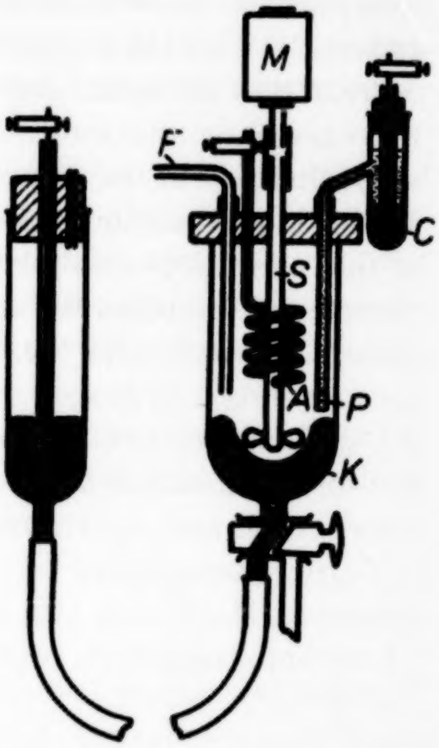

Fig. 3. Titration cell according to LINGANE[15] for controlled potential coulometric determinations. K = mercury cathode; A = silver anode; C = calomel electrode; S = stirrer; F = tube for introducing solution to be titrated; P = porous glass disk.

In acid - base titrations resulting in a change of pH, the quantities of electricity can be measured very precisely up to 0.01 coulomb by means of the colour change of the suitable indicator.

The use of coulometry in acidimetric titrations is limited since the generation cathode first reduces those ions that are more easily reduced to metal than H^+ is to elementary hydrogen. DEFORD, PITTS AND JOHNS[3], therefore, modified the coulometric titration in such a way that a hydroxide titration solution can be prepared outside the solution being titrated and then allowed to flow slowly into the titration flask. FUCHS AND QUADT[13] put ion-exchange resins in the solution around the auxiliary electrode, where they remove products of electrolysis.

Coulometry with a controlled potential of the working electrode originated with HICKLING[14]. LINGANE[15] developed it further and also introduced the mercury cathode for reduction coulometry (Fig. 3). In coulometry with a controlled potential, the initial current strength falls exponentially to zero according to the relation:

$$i_t = i_o \cdot 10^{-kt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In this equation, i_t is intensity at a time t, i_0 is the strength of the initial current, and k is a constant.

The analysis is completed when the initial current strength falls to a value corresponding to practically complete conversion of the substance being determined to the reaction product. In most determinations of this type the current does not fall completely to zero, because the supporting electrolyte allows the flow of the so-called background current, and the initial current strength can not decrease beyond this value. Provided there are no definite indications to the contrary, it is assumed that current remains constant throughout the entire electrolysis, and a correction is only applied for this value. In this kind of coulometric measurements, a decrease of current to zero is indicative of the quantitative completion. Thus a reliable coulometer is needed that reports the current consumption during the entire titration, rather than one which measures the current strength and the time. LINGANE[15], on the basis of LEHFELDT's experience[16], recommends a hydrogen-oxygen coulometer as the most preferable with an error of 0.1%. LINGANE AND SMALL[17] also recommend a coulometer based on the titration of hydroxide liberated by the electrolysis of a solution of potassium bromide, using a silver anode and a platinum cathode.

Current integrators for this kind of coulometric determinations have also been proposed. MACNEVIN AND BAKER[18] recommend the graphical integration of the curve of current strength *vs.* time. Integrating eqn. (1) we get:

$$Q = \int_0^t i_t \, dt \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

where Q is the quantity of electricity consumed in the time elapsing from the beginning of the determination up to time t. Other symbols have the same meaning as given previously. By substitution and integration we get:

$$Q = \int_0^t i_0 \cdot 10^{-kt} \, dt = \frac{i_0}{2.303\,k} (1 + 10^{-kt}) \quad . \; . \; . \; . \; . \; . \quad (3)$$

If we plot time against log i, we obtain a straight line with slope —2.303 k, whose intersection for $t = 0$ is equal to log i_0. Thus, with the measurements of at least two values of the current intensity at two time intervals, it is possible to determine i_0 and k and thus the total flow of electricity. With this method it is possible to determine the total consumption of electricity during the coulometric measurement, without having to carry the electrolysis to completion.

LINGANE[15], in a discussion of this procedure, states that two measurements of the current intensity are sufficient. But for reliable determination of the shape of the curve it is necessary to have more data in order to attain the desired precision. Thus it is necessary to prolong the actual carrying out of the electrolysis for a longer period of time. The greatest advantages of coulometric procedure with constant voltage current were found in the determination of metals on the mercury cathode. For this purpose, LINGANE[15] proposed an apparatus consisting basically of a mercury electrode located in the cylinder with a side connection for current and mercury, while the calomel electrode is placed outside the cathode region.

With the aid of a silver anode and platinum gauze[15] as a cathode, it is possible to determine iodide in the presence of chloride and bromide; bromide, however, can be detected in the presence of chloride in only a limited range of concentrations. During the determination of chloride the potential must be maintained exactly constant. The limitations of this method must be considered in the determination of bromide and chloride in a mixture in which the formation of solid solution of silver bromide with silver chloride takes place. It is also possible to carry out oxidimetric determinations with a platinum anode[18].

The precision of coulometric titrations is at least comparable to the precision of volumetric titrations. Let us assume that we can work with an intensity of the generation current of 1 mA for a period of 100 sec, and measure time with a precision of ±0.1 sec. This corresponds to 100 mA sec, *i.e.* 0.1 of coulomb, which is equal to 1.036 microequivalents with an uncertainty of ±0.001 microequivalents; the precision, therefore, is better than 0.1%.

If we work with a consumption of 30 ml of 0.1*N* solution in volumetric analysis, the uncertainty of one determination is about 1 - 2 drops, that is about $5 \cdot 10^{-6}$ equivalents. which is equal to $\frac{5 \cdot 10^{-6} \cdot 100}{30 \cdot 10^{-4}} = 0.16\%$.

The substitution of coulometric determinations for chemical primary standards[19] in analytical chemistry is increasing, owing to the precision of the technique and reliability in establishing optimum conditions. Because of this, the Faraday constant has been redetermined by CRAIG AND HOFFMAN[20].

In primary coulometric processes, the determination of metals, especially of cadmium, lead, nickel and cobalt, by controlled potential coulometry is described in detail in the papers of LINGANE and his co-workers[21]. Nitro-compounds were successfully determined by SEASE[22] and TURJAN[23]. Traces of copper in paper chromatography[24] were determined by means of coulometry. LEWARTOWICZ[25] determined oxidizing substances that were produced by reduction of soluble products.

In secondary determinations, reactions based on the use of halogens as intermediate substances prevail. Sulfides, thiosulfates, selenium, phenols, salicylic acid, unsaturated fatty acids, etc., were determined in this way by many authors.

Oxidation of ferrous ions in the presence of cerous ions or manganous ions (TUTUNDŽIĆ AND MLADENOVIĆ[26]), and oxidation of thallous ions in the presence of ferrocyanide[27] have also been done by coulometry.

A mercury pool cathode was used for generation of titanous ions in the determination of ferric ions, vanadates and a number of organic dyestuffs[28]. Also, uranium in its tetravalent form, generated in solutions of uranyl sulfate, has proved to be an efficient reducing substance[29]. Metallic copper, plated onto the platinum electrode, acts as the coulometric reducing agent[30].

Coulometric determinations were successfully applied in gas analyses, especially of oxygen[31-33].

Insofar as this limited review of the coulometric methods[34] will permit a generalized statement, it can be said that measuring the amount of electricity used during an analytical procedure can be as useful as measuring a volume of titration solution or a volume of a gas, or the weighing of a precipitated substance.

SUMMARY

Two methods for performing coulometric determinations have been developed. Either the precise time of duration of the electrolysis is measured or the voltage is controlled. An indicator is necessary for the first method, while the end-point can be determined by the drop of the generator current to the so-called "background current" in the alternate way.

The constant current method usually requires amperometric indication, which may give an incorrect end-point when conditions are not completely suitable. Chemical indicators can sometimes be used. The controlled potential method requires no indicator, but a good coulometer and an instrument for retaining constant voltage are necessary.

Coulometric determinations are based on the reactions of the substances to be determined with halogens, using different oxidizing or reducing agents, and with acids or bases.

The degree of accuracy obtained using coulometric titrations corresponds to the volumetric analysis results. In addition, however, coulometry may permit an even greater accuracy, when applied under the proper conditions.

The major advantage of coulometry consists in the ease, with which, within the limits of the reaction, micro-quantities of the reacting substances can be determined.

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THE MILLICOULOMETRIC METHOD FOR *n*-VALUES

by

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INTRODUCTION

The technique of measuring the total current during electrolysis of a small amount of solution with a dropping mercury electrode has been used to determine the number of electrons involved in polarographic reduction processes. This technique has been called "Millicoulometry". Although millicoulometry should be ideally suited for the determination of the number of electrons involved in the reduction of irreversible systems at the dropping mercury electrode, it has been the experience of the authors and others working in this field[1-9] that many variables must be carefully controlled and unknown sources of error disclosed before reliable information can be obtained as in macrocoulometry[10,11,12]. It is the purpose of this study to discuss, in general, the method of determining *n*-values by millicoulometry, its advantages and disadvantages, the sources of error, an application of the method to the nitro-nitrosoguanidine system, and in conclusion propose some recommendations for future work.

PRINCIPLES

Millicoulometry involves, essentially, the measurement (direct or indirect) of the total current passed during the polarographic reduction of a compound at constant potential, the measurement of the amount of compound reduced by this current, and finally the calculation of n (the number of electrons per molecule involved in electrolysis) by application of Faraday's laws.

The expression of Faraday's law used in the calculation of *n*-values is:

$$n = \frac{c}{F\,m}$$

where c is the number of coulombs passed during the reduction, m is the number of moles of the depolarizer reduced by the passage of c, and F is the Faraday or 96,500 coulombs. Thus, one need only know the amount of electricity consumed and the amount of compound reduced by that quantity of electricity to directly determine an *n*-value.

Since very small currents are used in millicoulometry, one must work with small volumes of solution to affect a concentration change of reasonable magnitude. For example, using a volume of 0.3 ml of solution, a concentration change of 50% may be obtained in a 2-h electrolysis. The concentration change is usually determined by running a polarogram immediately preceding the start of the run and then again at the end of the run. If the step-height of the compound is proportional to concentration, then the equation for the number of moles reduced during an electrolysis may be given by:

$$m = \left(1 - \frac{H_2}{H_1}\right)KC$$

In this equation H_1 and H_2 are the step-heights before and after electrolysis, respectively (Fig. 1), K is the volume (ml) of solution, and C is the concentration (moles/ml) of the depolarizer in solution.

The determination of the number of coulombs passed is made by integration of the area under the current - time record[1]. The integration may be accomplished with electromechanical integrators[6], or by simply weighing the paper of the area under a chart-recorded polarogram or calculating the area with a planimeter. The use of electromechanical integrators would seem to be preferred for precision and simplicity.

ADVANTAGES AND DISADVANTAGES

The main advantage of the millicoulometric method lies in the fact that it is a direct and rapid technique for determining *n*-values under the same conditions as one operates in polarography; thus, the reduction occurs at the dropping mercury electrode. In the case of rate-controlled reactions, as so many organic reductions may be, the *n*-values obtained by macrocoulometry and millicoulometry may be different because the final reduction products at a well-stirred large cathode may not be identical to those obtained by electrolysis at the dropping mercury electrode[13]. In addition, millicoulometry appears to be a useful technique for determining *n*-values of compounds that hydrolyze or decompose rapidly. For example, in work on nitrosoguanidine, it was found that this compound hydrolyzed too rapidly to obtain a reliable diffusion coefficient experimentally. The equipment needed in millicoulometry is usually easy to assemble and the desired applied potential for the electrolysis may be supplied by a polarograph.

When electrolysis at the dropping mercury electrode is carried out long enough to effect a change in concentration of the depolarizer of reasonable magnitude, there is always the danger of the reduction products further reducing, oxidizing at the anode, or reacting with one another. However, there should be less danger of this in millicoulometry than in macrocoulometry if one carries out the electrolysis only long enough to give a measurable change in the concentration of original reducible material. Another possible disadvantage of millicoulometry may be its value with reversible systems. However, if one uses a divided cell, both reversible systems and complex electrode processes might be conveniently and precisely studied.

SOURCES OF ERROR

During electrolysis of such small volumes of solution as are employed in millicoulometry, the concentration of depolarizer surrounding the mercury drop may be less than that of the main body of the solution. Thus, at no time during an electrolysis may the current flow be assumed to be proportional to the concentration of the solution. This necessitates a thorough stirring of the solution before the concentration of depolarizer is determined. This tendency of the solution to be less concentrated at the drop compared to the main body of solution has been termed the "depletion effect" and has been cited as a source of error in millicoulometry[6]. However, with the integration technique of REYNOLDS AND SHALGOSKY[1], if concentration is determined only after adequate stirring, no error due to this cause should exist.

It is necessary that only the current that reduces the depolarizer be employed in the calculation of *n*-values. Thus, the current flow due to charging current and the reduction of trace impurities must be subtracted from the total current flow. This residual current may be considered as that current giving rise to the open deflections from the zero current line at 10 mm to 12 mm at point *A* in Fig. 1. The line at 12 mm may then be considered as the base from which concentration and current will be measured. The level of this residual current should be constant during an electrolysis.

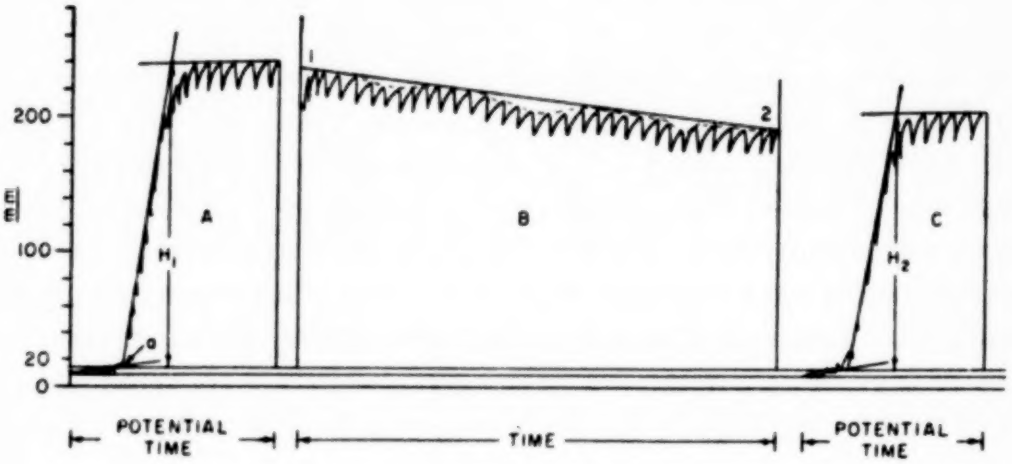

Fig. 1. Section of typical *n*-run.

A valid *n*-value for a particular compound may be obtained only if the reactions giving rise to its wave do not change during an *n*-run. Such changes in electrode reactions, due, possibly, to the increasing concentration of reduced species, may be detected by plotting the number of moles reduced at any time during the run against the number of coulombs passed during the same interval. Such a plot should yield a straight line passing through the origin and having a slope of $(nF)^{-1}$. If such a plot yields a curved line, a changing electrode process may be suspected. If the plot does not pass through the origin, constant errors in current calibration or concentration measurement may be responsible.

Sources of error in millicoulometry may be due to:

(1) Oxidation of a reduced species at the anode. This may be prevented by use of a divided cell, or use of an undivided cell using an anode other than the mercury pool.

(2) Electrolyzing over too long a period. This is especially important if the reduced species may undergo further slow reduction or react with the initial substance. In addition, the primary product might undergo some non-electrolytic transformation (as hydrolysis).

(3) Selection of an incorrect electrolysis potential. One should electrolyze on the limiting value of the diffusion current in order to obtain data pertaining to the entire process.

(4) Failure to meet usual polarographic requirements. Adequately buffered solutions should be employed and oxygen contamination must be removed and prevented.

(5) Use of mercury pool anode. Resolution of amalgam formed at dropping mercury electrode during electrolysis occurs more easily with this anode. The use of a separate anode (silver) affords good results. In addition, the choice of anode must be such that the reduction products or primary product can not react with the electrode.

EXPERIMENTAL

The apparatus used in this study for the determination of the *n*-values of *p*-nitroaniline, nitrosoguanidine, and nitroguanidine was a modification of the design used by REYNOLDS AND SHALGOSKY (Fig. 2). The assembly consisted of four principal parts. The beaker serves as a mercury reservoir to maintain constant mercury height within the microcell. The microcell, which is supported by a closely fitting plastic ring, serves as the actual cell and envelope to exclude oxygen. The microcell stopper is made by drilling holes in a frozen No. 11 solid-rubber stopper. This assures sliding fits of the various components. The stopper contains a flushing tube capillary, a capillary shoe (a device to eliminate vibration of the dropping mercury electrode), and a nitrogen inlet tube through which nitrogen is constantly passed during an *n*-run. The nitrogen used was obtained from compressed gas cylinders. Traces of oxygen present in the nitrogen were removed by passing the gas over copper turnings heated to 450°C. These traces of oxygen were removed whenever dilute solutions requiring high polarographic sensitivities were run. The cell and nitrogen atmosphere arrangement was such that no increase in residual current due to oxygen absorption occurred even after standing for 3 h. The flushing tube is drawn from 6-mm tubing and the right-angle bends

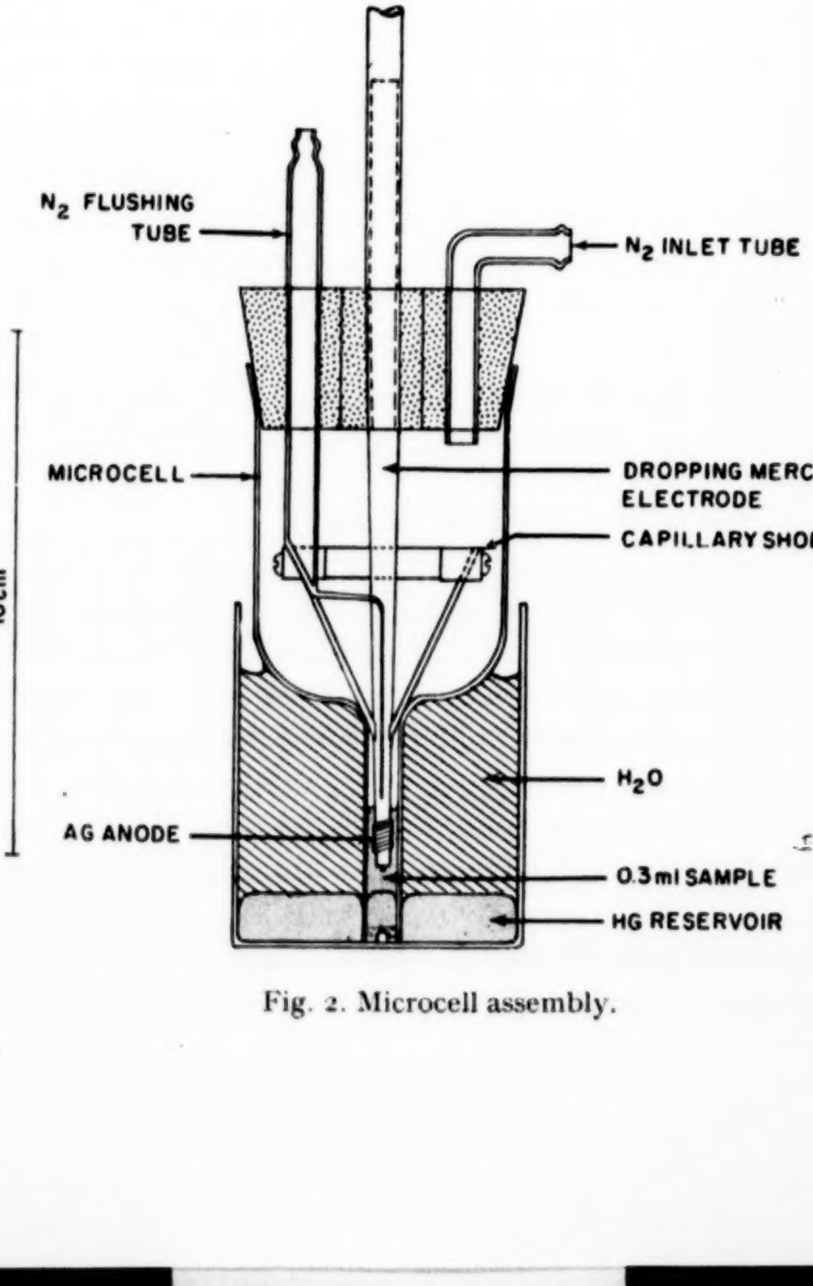

Fig. 2. Microcell assembly.

are made by heating the capillary with a very small flame and allowing the weight of the capillary to form the bend. The pressure for the flushing tube is achieved by a conventional variable water-height pressure regulator. Excess nitrogen is passed through the nitrogen inlet tube. The dropping mercury electrode is fabricated from commercial capillary tubing by tapering the tubing to an end diameter of 2 mm on a wet-belt sander. The electrode surface is polished in a lathe with carborundum powder of 150-500 grit. Four capillaries can easily be prepared in 2 h using this method. The authors' experience has indicated that capillaries prepared by this method are mechanically stronger and more likely to have constant drop rates than those prepared by drawing out marine barometer tubing in a flame. The silver anode is prepared from pure silver wire (0.020 in. in diameter) by winding into helical form to fit the capillary. A mandrel, shaped to the dimensions of the capillary, is used to form the anode. The windings are close and consist of a convenient number of turns (the authors used eight turns). Anodes prepared in this manner are almost identical. The anode is placed on the capillary to a height of 3 mm from the tip, and the end soldered to the copper wire winding on the capillary that leads to the polarograph anode terminal. The same capillary, stopper, and cell arrangement have been incorporated in a divided cell (Fig. 3). This divided cell is similar to that of MEITES[10].

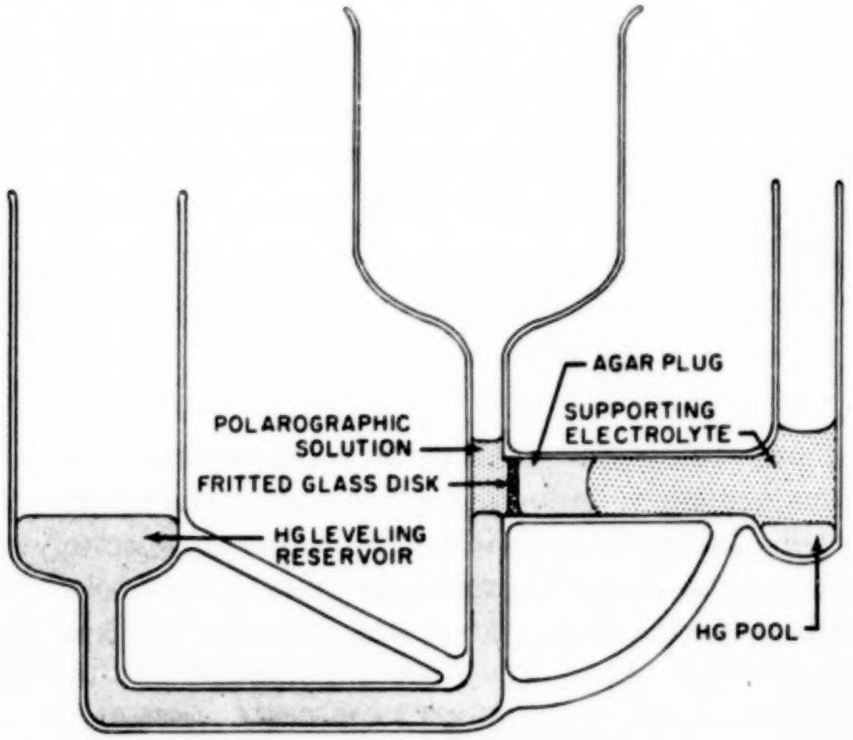

Fig. 3. Divided microcell assembly.

When one is working with irreversible systems, the supporting electrolyte should be well buffered. The successful use of a silver anode depends upon the formation of an insoluble silver salt during reduction. For this reason, KCl was present in all buffer solutions. Solvent systems that will form complexes or in any way affect the solvation of silver should not be used[16]. The position of the silver anode from the tip of the capillary did not appear to be critical. Anodes were changed frequently because they became amalgamated quite easily. The effect of amalgamation upon the polaro-

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graphic waves was not determined, but every effort was made to prevent use of an amalgamated anode.

The relationship between step-height and concentration was established in a polarographic cell using 10 ml of solution. After these calibration data were obtained, the beaker containing mercury was placed in a constant temperature bath at 30°C, the microcell was placed therein, and 0.30 ml of solution was then introduced by means of a graduated pipette. The apparatus was further assembled (Fig. 2) and the solution was flushed for 10 min. A polarogram was then obtained. The potential applied to the cell was held constant at a value lying on the more positive portion of the diffusion plateau. Between the running of the polarogram and the constant potential run, the chart was turned ahead by hand to allow space for calculation. During this time the dropping mercury electrode (DME) was removed from the circuit by means of the switch provided in the instrument. After setting the instrument to the desired potential, the DME switch and the chart motor were turned on simultaneously. When reduction had proceeded for 1/2 h, the chart motor and the DME switch were turned off simultaneously. The solution was again flushed for 5 min and a polarogram obtained. Since the voltage axis of the polarogram is also a time axis, integration of these polarograms may be carried out in the same manner as was employed with the constant voltage section (Fig. 1).

An alternate method, which may be used to advantage in the case of compounds producing only a single wave, is that of not running an initial and final polarogram, but taking the current at constant potential immediately after flushing as being proportional to concentration. This method simplifies the calculations considerably.

The undivided microcell and silver anode were employed in all work. The drop rate of the capillary was approximately 5 sec/drop at —1.2 V (applied to cell) in pH 10 Clark and Lubs' buffer[17] (2 ×).

RESULTS AND DISCUSSION

p-*Nitroaniline*

The standard chosen to test the method was *p*-nitroaniline (PNA). This compound requires 6 electrons per molecule for reduction and was investigated by REYNOLDS AND SHALGOSKY, who employed 0.1*N* KCl as the supporting electrolyte. The guanidine compounds under consideration had previously been studied polarographically at pH 10 in a Clark and Lubs' buffer. This system was chosen for PNA so that a direct comparison of *n*-values could be made. The PNA was crystallized three times from water and melted through the range 146.0-146.5°C.

The buffer solutions were prepared from reagent grade chemicals. Table I lists the *n*-values obtained with *p*-nitroaniline using the integration method and the 6/7 peak current method[14]. Each of the *n*-runs was for 1/2 h. These data were obtained at a residual current potential of —0.6 V applied to the cell and —1.2 V at the diffusion current plateau.

The range of results for each section is greater than the range in *n*-values between runs because the method depends upon the measurement of a difference in concentrations. Thus, if the initial concentration in Fig. 1 is such that H_1 is 200 mm, which was usually the case, then the step-height after the first 1/2-h section of reduction (H_2) would be approximately 200—(1/4 × 50% × 200) or 175 assuming a 50% reduction after

TABLE I

n-VALUE RESULTS OF *p*-NITROANILINE, pH 10

$c \cdot 10^1$	$m \cdot 10^7$	n-*Values obtained per section*					*vol. used (ml)*
		1	*2*	*3*	*4*	*n*	
1.430	2.471	6.32	5.78	6.14	5.57	6.00[a]	0.30
1.648	2.789	6.35	5.87	6.28	5.94	6.12[a]	0.45
0.8465	1.382	6.31	5.95	6.36	6.97	6.34[b]	0.45
0.6740	1.223	5.28	5.97	5.89	5.79	5.71[b]	0.30

[a] 1.6 m*M*
[b] 0.8 m*M*

four 1/2-h sections. This difference of 25 mm, corresponding to the reduction in concentration during the first section, is subject to a 2% error in the 200- and 175-mm step-heights. Thus, an error of as much as 8 mm may be incorporated in this difference which is more than 30% error for that section. For this reason, it is best to carry out a number of sections of reduction.

The residual current for these data was measured at —0.6 V applied to the cell and was initially about 13 mm in height (the zero-current position was 10 mm). An increase in this residual current was observed after each section of reduction in all the *n*-runs with PNA at pH 10.0. This increase in residual current did not occur in equal increments, but increased rapidly to a constant value. Thus, at the beginning of the third section, the residual current was usually 22 mm; but at the end of the fourth section it had increased to only 25 mm. Attempts to discover the cause of this increase in residual current were unsuccessful. No such increase has been noted during the identical treatment of the buffer solution alone, indicating that this increase is directly related to the reduction of the PNA. This conclusion is supported further by the fact that reductions with nitro and nitrosoguanidine in this system showed no increase in residual current.

Nitroguanidine

From study of the data obtained with *p*-nitroaniline it was decided that the millicoulometric method as employed here should provide satisfactory data with the nitro-nitrosoguanidine system. Therefore, nitroguanidine was investigated in a Clark and Lubs' buffer of pH 10. Polarographically, nitroguanidine produces a single, well-defined wave at this pH. Table II presents the *n*-values obtained. The residual current was measured at —0.86 V applied to the cell and the diffusion current at —1.58 V.

TABLE II

n-VALUES OF NITROGUANIDINE, pH 10.0

Initial conc. (mM)	$c \cdot 10^2$	$m \cdot 10^7$	*n-Values obtained per section*				
			1	*2*	*3*	*4*	*n*
1.36	8.154	1.951	4.31	4.91	5.23	4.88	4.76
1.24	6.675	1.496	4.84	5.52	5.29	—	5.08
1.44	7.303	1.561	5.24	5.11	6.29	4.92	5.33
2.40	18.91	3.855	5.20	4.87	5.07	5.23	5.09
2.40	15.07	3.123	4.63	5.32	5.19	—	5.00

Samples of 0.3 ml were used in all runs. The data indicate that nitroguanidine reduces by means of a 5-electron-per-molecule reduction process at the dropping mercury electrode in this pH 10 medium. Thus, the reduction of nitroguanidine in this case does not appear to be a simple process, but may be explained by a coupling of the products of a 2- and 6-electron reduction (Fig. 4). Since nitroguanidine has been investigated and found to reduce directly to aminoguanidine in acid solution[18], a 2.5-m*M* solution of the compound was studied in 6*N* HCl. An average *n*-value of 6.35 was obtained in this medium.

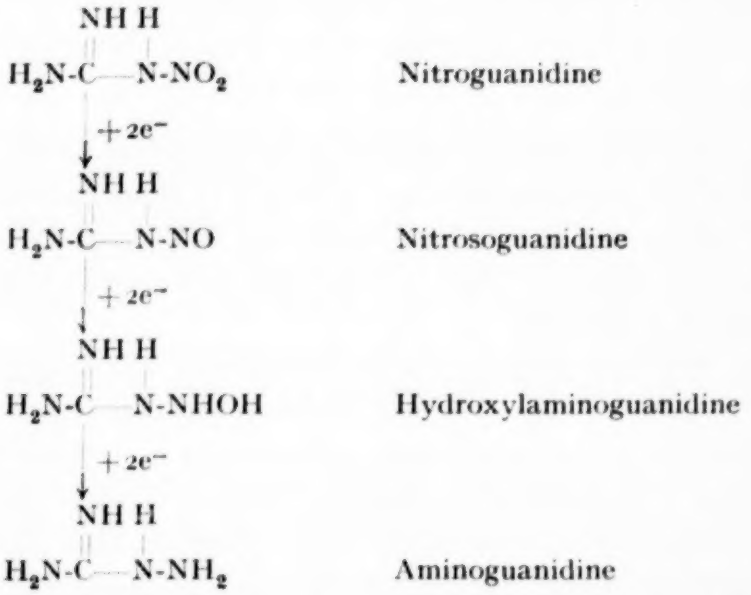

Fig. 4. Possible reduction mechanism for the nitro-nitrosoguanidine system.

Nitrosoguanidine

An investigation of this compound was also made in a Clark and Lubs' buffer of pH 10. The oxidation state of nitrosoguanidine differs from that of nitroguanidine by 2 electrons per molecule (Fig. 4). Thus, the *n*-value of nitrosoguanidine would be expected to be 2 electrons per molecule less than that of nitroguanidine, if the reduction process of nitroguanidine passed through nitrosoguanidine. This was shown to be the case. The results are shown in Table III. Considered separately, the value of 3 electrons per molecule of nitrosoguanidine is as difficult to interpret as the 5 electron value for nitroguanidine. However, the difference of 2 electrons between the reductions appears to indicate that the reduction of nitroguanidine to nitrosoguanidine is a fairly straightforward process, and that the odd numbered electron changes are the result of somewhat complex processes occurring beyond the nitroso state.

TABLE III

n-VALUE OF NITROSOGUANIDINE AT pH 10

Initial conc. (*mm*)	% *Reduction*	$c \cdot 10^3$	$m \cdot 10^7$	*n*
4.0	35.3	10.922	4.270	2.89
4.0	41.9	13.604	5.041	3.06
4.0	47.8	15.898	5.738	3.13
4.0	49.9	15.749	6.034	2.96
0.4	54.5	1.920	0.656	3.31

CONCLUSIONS

Although the millicoulometric method appears, and has been shown by some workers in the field, to give reliable data for *n*-values, it is the conclusion of the authors that many known variables must be carefully controlled and some hidden factors yet disclosed before this method can be trusted implicitly. Since this method appears to be ideally suited for irreversible reductions and for studying reactions at the dropping mercury electrode, it would be a great aid to those working in the field if further research could confirm its potentiality. With this in mind, the following recommendations for future work in millicoulometry are proposed.

(1) Methods of coulomb measurement should be critically examined with acceptable standards and applied to millicoulometric studies.

(2) Methods of concentration measurement not dependent upon the polarograph should be investigated.

(3) Apparatus should be designed and evaluated as to reliability for *n*-values.

(4) Similar millicoulometric studies of organic compounds should be made. Effect of pH, concentration, and supporting electrolyte should be critically examined.

(5) Compare reactions (*n*-values) occurring at a large mercury electrode with those at a dropping mercury electrode.

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SUMMARY

Millicoulometry as applied to the determination of *n*-values has been discussed in general with emphasis on its advantages and disadvantages, the main sources of error, and an application of the method to the nitro-nitrosoguanidine system. Results are discussed and recommendations for future work in the field are proposed.

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COULOMETRIE UND DAS COULOMB ALS UNIVERSELLE URTITERSUBSTANZ

von

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Die Chemie hat etwa hundert Jahre gebraucht, um auf den von Faraday geschaffenen experimentellen Grundlagen eine neue und vielseitige analytische Methode aufzubauen und zu entwickeln, eine Methode die, wie es uns scheint, uns ermöglichen kann auch an unseren längst gewohnten Grundmassen nutzbringende und zweckentsprechende Änderungen vorzunehmen. Es kann als ein klassisches Beispiel dienen, wie eine experimentelle Erkenntnis, die zu gleicher Zeit auch die theoretischen Grundgesetze einer neuen Wissenschaft ergab, auf einen gewissen Stand der theoretischen und technischen Entwicklung und auf zeitgemässe Bedürfnisse warten musste, bevor sie zur Grundlage auch eines neuen Gebietes der analytischen Chemie wurde, durch Schaffung der coulometrischen Arbeitsweise.

Die coulometrischen Bestimmungen, die zuerst von SZEBELLÉDY UND SOMOGYI (1938) konsequent durchgeführt wurden, ohne hier auf ihre einzelnen Vorgänger einzugehen, haben ihre weitere Entwicklung erst von 1945, also seit kaum mehr als zwölf Jahren angetreten, und heute kann man sagen, dass wir schon coulometrisch sicher und genau auf allen Gebieten der klassischen Volumetrie arbeiten können, ausserdem konnten auch neue Arbeitsgebiete durch die coulometrische Arbeitsweise erschlossen werden, was wohl durch die klassischen Methoden schwer auszuführen wäre.

Die Coulometrie, die uns seit mehreren Jahren beschäftigt, stellt, unserer Meinung nach, aus mehreren Gründen, elektrochemisch und analytisch, ein sehr interessantes Arbeitsgebiet dar.

Erstens werden durch coulometrische Studien der analytischen Chemie neue Wege und neue Gebiete auf Grund der Untersuchung primärer und sekundärer Anoden- und Kathodenvorgänge, insbesondere in Bezug auf die Vollständigkeit der betreffenden elektrochemischen oder chemischen Umsetzung, wofür bis vor kurzem kein Interesse herrschte, gewiesen und erschlossen. Durch die Möglichkeit sehr genauer Abmessung und Dosierung der Elektronen, bzw. der Coulombs — was heutzutage vollkommen automatisiert worden ist und uns in die Lage versetzt auch bis auf Mengen elektrolytisch erzeugter Substanzen bis zu 10^{-17} Grammäquivalenten hinunterzugehen und buchstäblich einige zehn Elektronen in der Sekunde zu zählen, sie zu beherrschen und mit ihnen mit grosser Genauigkeit zu operieren — konnten wir verschiedene Mikro- und Submikromethoden entwickeln und mit Erfolg anwenden.

Auf dieser Weise, stellen die coulometrischen Bestimmungen nicht nur eine Bereicherung der analytischen Chemie und eine Erweiterung ihres Arbeitsgebietes dar, sondern ermöglicht uns die coulometrische Denk- und Arbeitsweise auch die Ab-

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steckung neuer weitreichender Ziele und drängt uns dazu, qualitativ ganz neue Fragen zu stellen. Die, in relativ kurzer Zeitspanne, erzielten Erfolge und Resultate der coulometrischen Bestimmungen haben auch einen prinzipiellen Einfluss auf die Lösung analytischer Fragen ausgeübt, wobei die Einfachheit und Eleganz und hauptsächlich die Vielseitigkeit der Anwendungsmöglichkeiten der coulometrischen Arbeitsweise, auch rein elektrochemischer Reduktionen und Oxydationen, die grosse Sicherheit und Sauberkeit beim Arbeiten mit kleinsten Mengen, sowie die grösst mögliche Ausschaltung des subjektiven Einflusses, eine ausschlaggebende Rolle spielen. Nicht zu unterschätzen ist dabei auch noch die Möglichkeit der Vermeidung der Zugabe von Substanzen die oft sehr störend wirken können.

Auf Grund der bisherigen Ergebnisse sind wir schon in der Lage, zu zeigen, dass ausser den rein analytischen Anwendungen der coulometischen Arbeitsweise, wir im Begriffe sind, auch noch andere Arbeitsgebiete der Coulometrie zu erschliessen und durch die Coulometrie zu neuen Erkenntnissen und Fragestellungen zu gelangen, die wir am Ende unserer Ausführungen auch kurz streifen werden können.

Ohne zeitliche Möglichkeit auf die Arbeiten, um nur einige zu nennen, die von BROWN UND SWIFT, FARRINGTON, FURMAN, EPSTEIN, CAMPBELL, CARSON, COOKE, DE FORD, LINGANE, MYERS, MACNEVIN, REILLEY und ROGERS, sowie von CHARLOT, GAUGUIN und BADOZ-LAMBLING ausgeführt und auch weiter betrieben werden, in der volumetrischen Acidimetrie und Alkalimetrie, der Jodo-, Chloro-und Bromometrie, Cerrimetrie, Kuprometrie und Ferrometrie, näher einzugehen, möchten wir kurz unsere Methoden, die wir mit unseren Mitarbeitern ausgeführt haben und die wir weiter entwickeln, vorlegen und die Resultate unserer eben abgeschlossenen Arbeiten mitteilen, die es uns ermöglichen auch grundlegende Fragen anzuschneiden.

Mit unseren Mitarbeitern MLADENOVIĆ, STOJKOVIĆ, DOROSLOVAČKI, JANJIĆ-TATIĆ, PAUNOVIĆ, PAUNOVIĆ UND MLADENOVIĆ haben wir einige neue Gebiete der analytischen Chemie der coulometrischen Arbeitsweise erschlossen und arbeiten zurzeit an dem weiteren Ausbau und der Anwendung der Grundmethode.

Auf dem Gebiet der coulometrischen Acidimetrie und Alkalimetrie haben wir, als eine Abart, die von uns so benannten „indirekten coulometrischen Bestimmungen" geschaffen und zwar in zwei Varianten. Erstens konnten wir, um ein Beispiel zu nennen, Kupfer coulometrisch indirekt in saurer Lösung durch gleichzeitige Abscheidung des Metalls und des Wasserstoffs, in vorher coulometrisch geeichter saurer Lösung, bestimmen, wodurch eine prinzipiell neue Möglichkeit geschaffen wurde Metall-Ionen in Mengen von einigen mg und darunter coulometrisch acidimetrisch zu bestimmen, wobei die Eigenschaften des abgeschiedenen Metalls, wie wir durch variieren der Stromstärke und Stromdichte gezeigt haben, keinen Einfluss auf die Genauigkeit der Resultate ausüben, soweit die Lösung nach elektrolytischer Abscheidung der letzten Spuren der zu bestimmenden Metall-Ionen noch schwach sauer bleibt, um nachträglich bis zum Neutralisationspunkt coulometrisch titriert zu werden.

Zweitens, die Hydrolyse einiger Metallsalze in wässriger Lösung ausnützend, wie z.B. des Aluminiumsulfats, ist es uns gelungen, die durch Hydrolyse entstandene Säure coulometrisch zu titrieren und auf diese Weise, durch Störung des Gleichgewichtes, die Hydrolyse weiterzutreiben, bis zur restlosen Ausfällung des Hydroxyds und gleichzeitigen Bestimmung der gesamten, vorher am Metall gebundenen Säure. Diese Arbeitsweise stellt eine sehr schnelle, genaue und zweckmässige und breit anwendbare Methode der indirekten coulometrischen Bestimmung von Aluminium und anderen

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Ionen welche leicht hydrolysierbare Verbindungen bilden dar, analog den früher von KOLTHOFF volumetrisch ausgeführten Bestimmungen. Wir sind zurzeit bemüht die Solvolyse allgemein in verschiedenen Lösungsmitteln, nach der gleichen Arbeitsweise, für verschiedene analytische und andere Zwecke weiter zu entwickelen, was uns ermöglicht die hydrolytischen und solvolytischen Vorgänge auch coulometrisch anzugreifen.

Das nähere Studium der coulometrischen Acidimetrie und Alkalimetrie ermöglichte uns auch die Wanderung der Wasserstoff-Ionen in verschiedenen Medien, die zwischen den Elektroden eingeschaltet sind, zu verfolgen, wodurch erstens eine kritische Abänderung der Arbeitsweise in der Acidimetrie resultierte, zweitens die Menge der abgewanderten Wasserstoff-Ionen mit der Zeit bequem bestimmbar gemacht wurde.

Es sei dabei noch eine praktische Anwendung der coulometrischen Acidimetrie und indirekten Acidimetrie erwähnt, die wir jüngst zustande gebracht haben. Es handelt sich nämlich um die Bestimmung der temporären Härte des Wassers, die coulometrisch bequem ausführbar ist. Hier möchten wir bemerken, dass wir dadurch auch Alkali- und Erdalkali-Kationen haben indirekt bestimmen können, durch coulometrische Rücktitration der zur Neutralisation nicht verbrauchten, vorher zugegebenen Säure. Es scheint uns, dass die genaue Abmessung der benötigten Coulombs bei der Härtebestimmung des Wassers, die Möglichkeit bietet, und den neuen Weg weist, die Härte nicht mehr durch die heute üblichen Grade, d.h. durch die Masse der vorhandenen Oxyde, auszudrücken, sondern durch die Anzahl der benötigten Coulombs, was, unserer Meinung nach, ein universelleres und eindeutigeres Mass darstellt, das unseren heutigen Möglichkeiten mehr entspricht.

Die coulometische Arbeitsweise weiter entwickelnd, konnten wir, gleichzeitig mit RAMSEY, FARRINGTON UND SWIFT und DEFORD, PITTS UND JOHNS, und unabhängig von ihnen, die coulometrische Jodometrie entwickeln, die, wie unsere bisherigen weiteren Anwendungen und die Arbeiten anderer Forscher zeigen, eine wirklich ausgezeichnete Möglichkeit bietet, durch elektrolytische Oxydation des Jod-Ions in wässriger Lösung, das nötige Jod quantitativ in jenem Augenblick zu schaffen, wann man es benötigt. Das heisst, ohne gezwungen zu sein, es vorher vorzubereiten und ständig den Titer der bereiteten Lösung nachzuprüfen. Unsere Anwendungen der coulometrischen Jodometrie haben unsere schon vorher ausgedrückte Meinung bestärkt, dass wir in der coulometrischen Jodometrie die Möglichkeit haben sämtliche jodometrischen Bestimmungen nur noch auf Grund der coulometrischen Eichung der Lösungen auszuführen, soweit sie noch unvermeidlich sind, wie z.B. in Kontroll- und Betriebslaboratorien und im Unterricht.

Durch das Studium der Oxydationspotentiale an indifferenten Anoden in sauren Lösungen von Mangansulfat, bei verschiedenen Konzentrationen und verschiedenen Mengenverhältnissen der Schwefelsäure und des Mangansulfats, durch Anwendung verschiedener Stromdichten, konnte das Gebiet der Konzentrationen und der Oxydationspotentiale abgegrenzt und theoretisch begründet werden, in welchen es zur quantitativen Bildung von Permanganat-Ionen kommt, was als Grundlage dienen konnte, auf welcher wir auch die coulometrische Permanganatometrie begründen und ausbauen konnten. Die bisherigen Anwendungen der coulometrischen Permanganatometrie zur Bestimmung von Oxalat-, Ferro- und Arsenit-Ionen, sowie zur Bestimmung von Wasserstoffperoxyd, bis zu Mengen von 1 mg, haben den Beweis erbracht, dass es vollkommen unnötig und unzweckmässig wäre auch weiter noch mit Lösungen, bereitet durch Abwägen von gereinigtem Kaliumpermanganat, dessen Titer immer

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wieder und unvollkommen bestimmt und kontrolliert werden soll, zu arbeiten, wo doch die coulometrische Arbeitsweise eine zuverlässige und saubere Möglichkeit bietet das Permanganat nach Bedarf herzustellen und zu gebrauchen. Wenn es schon noch immer unvermeidlich ist, in verschiedenen Laboratorien und bei verschiedenen Gelegenheiten mit Permanganatlösungen zu arbeiten, so sollte man sie wenigstens über Oxalsäure durch coulometrisch hergestelltes Permanganat eichen und auf diese Weise auch in die Permanganatometrie das Coulomb als Grundmass, als Urtitersubstanz, einführen und gebrauchen.

Ausser diesen beiden elektrolytischen Oxydationen, die eine besondere Bedeutung für die Ausdehnung der coulometrischen Arbeitsweise auf zwei wichtige Arbeitsgebiete der analytischen Chemie haben, bezwecken weitere Arbeiten auch andere analytisch interessante und coulometrisch anwendbare elektrolytische Oxydationen zu bearbeiten, die Bedingungen theoretisch festzulegen und experimentell auszuarbeiten um Perjodat-, Perborat-, Persulfat-, Perchlorat-Ionen und Bichromate elektrolytisch quantitativ oder mit konstanter Ausbeute herzustellen, um sie für verschiedene coulometrische Oxydationen zu gebrauchen und darauf neue coulometrische Methoden aufzubauen.

Ein besonders interessantes und vielseitig ausbaufähiges allgemeineres Gebiet der Coulometrie, stellt, unserer Meinung nach, die „coulometrische Metallometrie" — wie wir sie benannt haben — dar, die uns die Möglichkeit bietet durch anodische Auflösung verschiedener Kationen, sowie durch ihre gleichzeitigen Umsetzungen mit verschiedenen Anionen, mit denen sie schwerlösliche Verbindungen bilden, vielfältige bequeme und genaue coulometrische Bestimmungen auszuführen.

Gleichzeitig mit NAKANISHI UND KOBAYASHI, nach LINGANE UND SMALL, sowie MACNEVIN, BAKER UND MCIVER, die mit begrenztem Potential gearbeitet haben, konnten wir nach dem schon früher angegebenen Prinzip die coulometrische Argentometrie entwickeln und zeigen, dass man durch diese Arbeitsweise auch Mengen von Halogen-Ionen unter 1 mg mit Adsorptionsindikatoren sehr genau, schnell und bequem bestimmen und die ganze volumetrische Argentometrie auf dem Coulomb aufbauen kann, als auf der universellen Urtitersubstanz, das schon mit Silber als Messgrösse für das internationale Ampere in Beziehung steht.

In weiterer konsequenter Entwicklung desselben Grundgedankens wurde unsererseits auch die coulometrische Plumbometrie ausgearbeitet und für die Bestimmung von Chromat, Bichromat, Ferrocyanid, Oxalat, Sulfat, Molybdat und Wolframat, mit amperometrischer Bestimmung des Endpunktes, oder auch durch Anwendung von Adsorptionsindikatoren, angewandt. Es zeigte sich dabei, dass man bei Einhalten bestimmter Bedingungen, sehr genau und schnell, serienmässige Bestimmungen von mehreren Anionen, in Mengen von 1 mg bis 50 mg ausführen kann, wobei die Plumbo-Ionen durch ihre spezifischen Eigenschaften und kleinen Löslichkeitsprodukte der gebildeten Verbindungen in vielen Fällen sich als sehr geeignet gezeigt haben.

Als nächstes Metall für die coulometrische anodische Auflösung für metallometrische Zwecke hat das Quecksilber unser Interesse erregt und wir konnten auch durch das Studium der elektrolytischen Lösungserscheinungen die Bedingungen auffinden, unter denen das Quecksilber glatt quantitativ als Merkuro-Ion in Lösung geht, und mit vorhandenen geeigneten Anionen schwerlösliche Verbindungen bildend, es ermöglicht dieselben coulometrisch-metallometrisch genau und sehr bequem zu bestimmen. Auf diese Weise konnten wir Chlor-, Brom-, Jod-, Oxalat-, Jodat-, Molybdat- und

Chromat-Ionen mit amperometrischer Endpunktsanzeige bestimmen, was uns gleichzeitig die Möglichkeit bietet durch Auswahl geeigneter Kationen, die wir coulometrisch in Lösung bringen, je nach den herrschenden Bedingungen und Bedürfnissen, zur beabsichtigten Fällung zu gebrauchen und auch miteinander zu kombinieren. Da sich unter den Merkuroverbindungen viele analytisch wichtige vorfinden, ist gerade die coulometrische-metallometrische Verwendung des Quecksilbers für die Lösung analytischer Aufgaben sehr interessant.

Die coulometrische Metallometrie komplex betrachtend und weiter ausbauend, haben wir, theoretisch und experimentell, auch die Bedingungen für die Einführung des Kupri-Ions in die Metallometrie ausgearbeitet, was uns jüngst gelang. Die Auflösung des Kupfers in Form von Kupri-Ionen geht glatt vonstatten und wir gebrauchten es, um ein Beispiel anzuführen, zur Bestimmung der Anthranilsäure mit amperometrischer Endpunktsanzeige.

Auf Grund der bisher gesammelten Erfahrungen auf dem Gebiete der coulometrischen Bestimmungen, hauptsächlich der coulometrischen Metallometrie, konnten wir die coulometrische Arbeitsweise in noch anderen Richtungen ausbauen und auch zur Lösung nicht rein analytischer Probleme auswerten. Es hatte sich, erstens, der von uns gefasste Gedanke als richtig erwiesen, durch coulometrische Metallometrie nicht nur quantitative Bestimmungen auszuführen, sondern auch die Möglichkeit zu schaffen, aus Gemischen verschiedener Isomeren, diejenige Komponente, durch metallometrische Ausfällung, zu trennen, welche ein schwerlösliches Salz mit dem metallometrisch in Lösung gebrachten Kation bildet, wofür nach unserer bisherigen Erfahrung schon mehrere Kationen zu Verfügung stehen, deren Anzahl sich wahrscheinlich beträchtlich vermehren wird. Durch diese Anwendungsmöglichkeit, verschiedene Isomeren voneinander zu trennen und gleichzeitig auch ihren Gewichtsanteil mit guter Genauigkeit zu ermitteln, kann die coulometrische Metallometrie auch für präparative Zwecke Wichtigkeit erlangen und eine ziemlich ausgedehnte Anwendung finden.

Durch diese Arbeiten, die uns meistens zu den komplexen metallorganischen Verbindungen führten, stellte es sich heraus, dass die coulometrische Arbeitsweise gleichzeitig auch geeignet sei, die Kinetik der Komplexbildung zu studieren, da das fast unmittelbare Zählen der in der Zeiteinheit in Lösung übergeführten Kationen eine bequeme und sichere neue Möglichkeit darstellt, die Geschwindigkeit der Vorgänge zu verfolgen, und zwar nicht nur auf diesem begrenzten Gebiet der Komplexbildung, sondern auch im allgemeinen.

Schliesslich, in vielen Fällen, wo es geboten ist irgendeine chemische Umsetzung bei einem bestimmten Wasserstoffionenexponenten ablaufen zu lassen und das pH dabei konstant zu halten, kann man anstatt chemischer Puffer, die in ihrer Wirkung begrenzt, und auch nicht immer in geeigneter Form anwendbar sind, die coulometrische Pufferung einführen, die es uns ermöglicht, synchron mit der Säure- oder Basebildung, diejenigen Ionen herauszuelektrolysieren, die einen ungünstigen Einfluss auf das konstant zu haltende pH ausüben können. Da uns auf diese Weise, durch Regelung der Stromstärke, mittels der coulometrischen Pufferung auch die Geschwindigkeit der Säuren- oder Basenerzeugung erfassbar geworden ist, können wir, neben der praktischen Bedeutung der coulometrischen Pufferung für das Laboratorium und den Betrieb, dieselbe auch zur Bestimmung der Reaktionsgeschwindigkeit, nützlich und sehr vielfältig verwenden und weiter entwickeln.

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Durch diese kurz beschriebenen Anwendungen der coulometrischen Arbeitsweise zur Bestimmung und Trennung verschiedener Isomeren, sowie für ihre präparative Darstellung, für die coulometrische Pufferung in mehreren Richtungen und zum Studium der Kinetik verschiedener Umsetzungen, glauben wir die eingangs aufgestellte These bewiesen zu haben, dass, ausser zu analytischen Zwecken, die coulometrische Arbeitsweise auch in anderweitigen Anwendungen noch sehr mannigfaltig ausgebaut und weiter entwickelt werden kann und, dass wir mit ziemlicher Berechtigung erwarten können, dass sie bald eine weit grössere Verbreitung finden wird.

Bei der Ausarbeitung der vorgetragenen Abarten der coulometrischen Acidimetrie und bei der Schaffung der coulometrischen Jodometrie, coulometrischen Permanganatometrie und der coulometrischen Metallometrie sind wir zu der Überzeugung gelangt, dass die coulometrische Arbeitsweise bei den heutigen Möglichkeiten der Handhabung und der Abmessung von Coulombs uns dazu führt die volumetrischen Standardlösungen nur noch coulometrisch zu eichen und das Coulomb, anstelle der Masse einer chemischen Substanz, als universelle Urtitersubstanz in die Volumetrie und in die gesamte analytische Chemie einzuführen. CRAIG UND HOFFMAN haben unlängst, durch Präzisionsmessungen der elektrolytischen Oxydation von Natriumoxalat, den mittleren Wert der Faraday Konstante zu 96492 ± 3 absoluter Coulombs pro Äquivalent in chemischer Skala bestimmt, d.h. mit einem Fehler von ± 3 Coulombs, bzw. von 0.003 %, worin auch der Fehler der Abmessung der chemischen Materie mitenthalten ist. Daraus kann man ersehen, dass heute schon durch coulometrische Messungen, leicht eine Genauigkeit erreicht wird, die durch volumetrische Abmessung nur in bestimmten Laboratorien erreichbar ist, und welche, ausserdem, die sonst üblichen Arbeitsmethoden bei weitem an Genauigkeit, Sicherheit und Zuverlässigkeit übertrifft.

Die Wahl der Urtitersubstanz für eine bestimmte Gruppe von Bestimmungen, ist von jeher eine der schwierigsten Fragen der Volumetrie und stellt einen prinzipiellen und elementaren Mangel der volumetrischen Methode dar, da wir noch immer nicht über festgelegte und allgemein anerkannte Urtitersubstanzen verfügen, sondern für dieselben Zwecke verschiedene Ursubstanzen, oft nach Gewohnheit oder durch Autoritäten übernommen, gebrauchen. Ist es doch bezeichnend, dass auch heutzutage auf diesem Gebiete eine eifrige Forschung betrieben wird, deren Ziel es ist, neue und geeignetere Urtitersubstanzen für verschiedene Zwecke der volumetrischen Titration aufzufinden und bereitzustellen. Man sollte diese Arbeiten nicht nur als einen Drang nach Neuheit bezeichnen, sondern es wäre daraus der Schluss zu ziehen, dass der heutige Stand der Wissenschaft und der Praxis in dieser Hinsicht noch nicht in genügendem Masse befriedigend ist, wie es dem Fortschritt und den heutigen Möglichkeiten entsprechen könnte.

Zu dieser Unsicherheit in der Auswahl und Anwendung verschiedener Urtitersubstanzen, die voneinander abweichen und deren Anwendbarkeit auch von ihrer Abstammung abhängt, welche zugleich auch einen Mangel an Einheitlichkeit bekundet, gesellen sich auch die Fehlerquellen, und so kommt man zu einem Bild, das vieles zu wünschen übrig lässt, hauptsächlich bei Bestimmungen kleiner Mengen von Substanzen, und auch solchen, bei welchen ein hoher Grad der Genauigkeit angestrebt wird. Ohne eingehender die Operationen und die Fehlerquellen bei der Reinigung der Substanzen und der Bereitung volumetrischer Lösungen, die Erhaltung und ständige Prüfung, sowie die Berechtigung des Gebrauches verschiedener eingeführter Urtitersubstanzen zu behandeln, möchte ich nur kurz erwähnen, dass wir für die

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Acidimetrie und Alkalimetrie 66 verschiedene Urtitersubstanzen, nach bis in jüngste Zeit durchgesehener Literatur, ohne dabei Anspruch an Vollständigkeit zu erheben, feststellen konnten. Auf anderen Gebieten der Volumetrie ist die Zahl der Urtitersubstanzen bescheidener, aber immer noch genügend gross um zu zeigen, dass keine von ihnen vollauf befriedigt.

Dagegen hat man schon auf Grund der bisher ausgearbeiteten coulometrischen Methoden und Verfahren die Berechtigung, das Coulomb als einzige, universelle Urtitersubstanz, anstelle aller bisher gebrauchten Urtitersubstanzen, zum allgemeinen Gebrauch zu empfehlen, und zwar, in der Acidimetrie und Alkalimetrie, in der Jodometrie, Bromometrie und Chlorometrie, in der Permanganatometrie, in der Metallometrie, in der Cerrimetrie und auch sonst auf allen anderen Arbeitsgebieten, die mit den erwähnten in einer bestimmten Beziehung stehen, ohne dabei ausser Acht zu lassen, dass die Erschliessung auch weiterer bekannter, sowie ganz neuer Gebiete für die coulometrische Arbeitsweise noch bevorsteht und in vollem Flusse ist.

Nach Veröffentlichung unseres ersten diesbezüglichen Vorschlages haben schon mehrere namhafte Forscher die coulometrische Eichung und das Coulomb angewandt und weiter empfohlen, unter denen wir BADOZ-LAMBLING, GAUGUIN, ECKFELD UND KUCZYNSKY und AGASAJAN nennen möchten.

Auch wenn das Arbeiten mit Elektron, bzw. Coulomb, als universeller Urtitersubstanz nicht genauer wäre, als die Verwendung verschiedener und spezifischer chemischen Urtitersubstanzen, sollte man, unserer Meinung nach, das Elektron, bzw. das Coulomb als universelle und konstante Urtitersubstanz, unter allen Umständen, in die analytische Chemie einführen, um dadurch eine einheitliche und allgemein anwendbare internationale Grundlage für die gesamten volumetrischen, potentiometrischen, amperometrischen, konduktometrischen und sonstigen instrumentellen Titrationen zu haben.

ZUSAMMENFASSUNG

Es wurden die theoretischen Grundlagen und die neu geschaffenen coulometrischen Methoden, wie indirekte coulometrische Methode, coulometrische Jodometrie, coulometrische Permanganatometrie und coulometrische Metallometrie, mit den Anwendungen für die Bestimmung und präparative Trennung verschiedener Isomeren, für das Studium der chemischen Kinetik und für die coulometrische Pufferung, sowie die damit erzielten Resultate und die mögliche weitere Entwicklung dargelegt.

Auf Grund der bisher erzielten Ergebnisse wurde auf die Möglichkeit und Zweckmässigkeit der Einführung des Elektrons, bzw. des Coulombs als einer universellen Urtitersubstanz anstelle zahlreicher verschiedenen chemischen Substanzen, als mehr oder minder berechtigten Urtitersubstanzen, in die analytische Chemie, ausdrücklich hingewiesen und der allgemeine Gebrauch des universellen Coulombs vorgeschlagen.

SUMMARY

The theoretical bases of coulometry are described as well as the newly developed coulometric methods, such as the indirect coulometric method, coulometric iodometry, coulometric permanganatometry, and coulometric metallometry. Furthermore the application of coulometric methods to the determination and preparative separation of various isomers, to the study of chemical kinetics and for coulometric buffering is dicussed; the respective results obtained are presented and the potential further development is indicated.

Based on the results mentioned, the possibility and usefulness is pointed out of the introduction in analytical chemistry of the electron or the coulomb, as a universal standard, instead of the numerous chemical substances, more or less suitable for this purpose, and the general use of the universal coulomb is proposed.

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DISKUSSION

Prof. G. VALENSI (Poitiers):

Il est hors de doute, du point de vue pratique, que les méthodes coulométriques conduisent dans beaucoup de cas, avec plus de commodité expérimentale, à une précision aussi grande que les méthodes gravimétriques. Je me réserve d'étudier la question de plus près, mais je n'ai pas l'impression qu'il en est toujours ainsi. Les recommandations de procéder par voie coulométrique pour déterminer le titre d'une solution standard primaire seraient donc parfaitement justifiées dans certains cas, mais il semble que dans d'autres, les recommandations de procéder par voie gravimétrique doivent être pour le moment maintenues.

Le sujet est très différent du point de vue des définitions données, qui doivent reposer sur des bases théoriques. Il fut un temps où il existait deux systèmes d'unités pratiques, le premier ayant d'ailleurs la préférence des experimentateurs: l'un était le système international, où le coulomb était précisément défini par une certaine masse (arbitraire) d'argent; la constante F de Faraday avait alors, par convention, une valeur bien déterminée. L'autre était le système absolu, où le coulomb était indirectement défini par voie électromagnétique: la constante F de Faraday était alors entachée d'une incertitude expérimentale, devenue moindre aujourd'hui mais toujours existante. Depuis quelques années cependant, le National Bureau of Standards, suivi par tous les physiciens du monde, a proposé avec raison de ne plus prendre en considération que le système pratique absolu, d'ailleurs maintenant devenu le système Giorgi, avec sa quatrième unité fondamentale, l'ampère (à laquelle se rattache facilement le coulomb) définie indirectement par voie électromagnétique. Si je comprends bien le Prof. TUTUNDŽIĆ, il nous propose de revenir en arrière, c'est à dire au fond à l'ancien système international, puisque, quelque soit la définition des standards titrimétriques utilisés, le résultat demandé d'une analyse doit être fourni gravimétriquement, par exemple en grammes par litre pour une eau minérale, ce qui, si l'on utilisait le système absolu, entraînerait l'erreur due à l'incertitude de la constante de Faraday. En fait, c'est une faute de principe que de baser la définition d'une grandeur uniquement rattachée aux dimensions fondamentales masse et longueur, sur la quatrième dimension du système Giorgi.

Il ne saurait en être autrement pour les titres des liqueurs qui servent d'intermédiaires pour obtenir cette grandeur et je juge, donc, pour conclure, que sans exclure aucune méthode coulométrique pratique pouvant être commode à sa mesure, la teneur d'une solution standard primaire doit être *définie* gravimétriquement et non coulométriquement.

Prof. P. S. TUTUNDŽIĆ:

Es ist für mich sehr angenehm, dass auch Sie der Meinung sind, dass die coulometrischen Methoden, auch experimentell bequemer, dieselbe Genauigkeit bieten, wie die gravimetrischen Methoden und dass mein Vorschlag, die coulometrische Methode zur Eichung der Standardlösungen einzuführen, in einigen Fällen wenigstens, berechtigt wäre.

Was aber die prinzipielle Frage einer absoluten Grundeinheit und die Frage des internationalen und des absoluten Systems betrifft, darüber liesse sich offensichtlich noch diskutieren.

Prof. A. OKAČ (Brno):

Prof. Tutundžić hat viele Erfahrungen in der Coulometrie und ich glaube, dass sein Entwurf der universellen Urtitersubstanz gut durchgedacht ist. Mir ist das ganz klar für einfache Reaktionen und ich möchte fragen, wie die Nebenreaktionen, Dismutationen usw. die Genauigkeit bei der Manganometrie beeinflussen? Doch müssen für Coulombbestimmung die chemisch reinen Substanzen (bzw. ihre Reinigung) beibehalten werden (besonders bei der Metallometrie).

Prof. P. S. TUTUNDŽIĆ:

Es freut mich sehr zu erfahren, dass Sie meinem Vorschlag für die Einführung einer universellen Urtitersubstanz zustimmen.

Selbstverständlich beeinflussen alle Nebenreaktionen die Genauigkeit der Bestimmungen, und zwar nicht nur bei der Permanganatometrie, sondern überhaupt, aber es wurde schon gezeigt, dass wir auch schon die Bedingungen kennen und neue schaffen können, unter denen die uns interessierenden Reaktionen mit wirklich hoher Genauigkeit ablaufen.

Prof. G. UNTERMANN (Frankfurt a/M):

Der Vorschlag des Redners ist sehr zu begrüssen. Kann man statt Coulomb das Wort „Aequivalent" einführen? Ist nicht auch die Bestimmung des Coulombs eine Gewichtsbestimmung?

Prof. P. S. TUTUNDŽIĆ:

Wenn es um das Wort „Aequivalent" ginge, könnte man es auch wohl auf Grund der funktionalen Beziehung des Coulombs zu einem bestimmten Teil des Aequivalents gebrauchen, obwohl ich nicht wüsste warum wir nicht beim Coulomb bleiben könnten.

Die Bestimmung des Coulombs ist in letzter Konsequenz auch eine Gewichtsbestimmung, aber es handelt sich nicht nur darum die Gewichtsbestimmung zu vermeiden, sondern viel mehr darum, anstelle zahlreicher Urtitersubstanzen eine universelle Grösse als Urtitersubstanz einzuführen.

Prof. P. DELAHAY (Baton Rouge, La.):

In addition to the difficulty of principle mentioned by Prof. VALENSI there is, it seems to me, a serious practical problem involved in the use of the Faraday as standard in titrimetric analysis. Electrode reactions which can be carried out with 100 per cent efficiency for *standardization* purposes are not numerous, and the Faraday has been determined by electrochemical methods for a very limited number of electrode reactions. Generation efficiency is often adequate for coulometric titrations but not standardization, *i.e.*, an efficiency of 99.9 per cent, is excellent for a coulometric titration but not for standardization. I believe that this constitutes a serious objection to Prof. TUTUNDŽIĆ's proposal.

Prof. P. S. TUTUNDŽIĆ:

Wenn auch zurzeit keine grosse Anzahl der Elektrodenreaktionen, die mit 100%-iger Genauigkeit durchzuführen wären, für die Standardisation bekannt ist, liegt das, unserer Meinung nach, nicht an der prinzipiellen Unmöglichkeit auch für noch andere Elektrodenreaktionen die Bedingungen für den quantitativen Ablauf festzulegen, sondern eher an noch nicht genügender Erfahrung und an bisherigem relativ kleinen Interesse am quantitativen Ablauf der elektrolytischen Oxydationen und Reduktionen.

Es scheint mir, dass man mit Genauigkeiten von 99.9% und darüber, die heute bequem erreichbar sind, und auch Ihrer Meinung nach, sich ausgezeichnet für coulometrische Titrationen eignen, zufrieden sein kann, aber ich erlaube mir auch darüber die Meinung, dass diese Genauigkeiten schon, durch Einführung des Coulombs als einer universellen Urtitersubstanz, auch für die praktische Standardisation der Lösungen viele Vorteile mit sich bringen würde.

Prof. I. M. KOLTHOFF (Minneapolis):

The atomic weight of silver remains fundamental as has been emphasized in the LAITINEN report of the Commission of Electrochemical Data of the Section of Analytical Chemistry of the IUPAC. The Coulomb can be a secondary standard only.

Prof. P. S. TUTUNDŽIĆ:

Ich habe den Eindruck, dass ich von Herrn LAITINEN in seinem Bericht der Komission für elektrochemische Grössen der Sektion der Analytischen Chemie der IUPAC nicht richtig verstanden wurde und kann mich mit seinem Bericht nicht einverstanden erklären.

Es bleibt wohl weiter, wie bisher, das Atomgewicht des Silbers als eine fundamentale Grösse bestehen, was ich auch in keinem Augenblick angezweifelt habe, aber ebenso, mit dem Atomgewicht des Silbers verbunden, bleibt auch als eine fundamentale Grösse das Coulomb, was auch schwer zu bezweifeln ist. Wenn man auch in Betracht ziehen kann, dass nach Jahren das elektrochemische Aequivalent und der Wert des Coulombs geändert werden könnten, so trifft dasselbe auch für die fundamentale Grösse des Atomgewichts des Silbers in gleicher Weise zu, weil sich auch diese Grösse mit dem Fortschreiten unserer Erkentnisse und unserer technischen Mittel zweifellos ändern kann, wobei diese beiden fundamentalen Grössen, das Atomgewicht des Silbers und das Coulomb doch so eng miteinander verbunden sind.

Wenn man die Relativität der beiden Grössen erkennt, ist es mir wirklich nicht klar, warum man lieber bei einer Unzahl von mehr oder minder genauen Urtitersubstanzen verharren und auch weiter z.B. nur für Acidimetrie und Alkalimetrie über 66 verschiedene Urtitersubstanzen mit mehr oder weniger Berechtigung und Erfolg gebrauchen soll, ohne auch von zahlreichen anderen Urtitersubstanzen für verschiedene andere Titrationen zu reden, wo man doch eine einzige universelle Urtitersubstanz, das Elektron, bzw. das Coulomb in die analytische Chemie einführen kann, dass uns neben bequemen und sicherem Arbeiten auch grosse Vorteile in der Einheitlichkeit mit sich bringt.

Ihre Meinung, dass man das Coulomb als sekundären Standard gebrauchen kann, bedeutet einen sehr ernsten Schritt vorwärts, in der Richtung der Einführung des Coulombs als einer universellen und allgemein anerkannten Urtitersubstanz, die uns von der bedrückenden Anzahl chemischer Urtitersubstanzen wird bald befreien können.

ADSORPTION KINETICS AND ELECTRODE PROCESSES

by

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This investigation has been published elsewhere[1], and consequently only a summary will be given here for reference in the discussion section.

PART I

The kinetics of adsorption on electrodes are studied for substances which are not reduced or oxidized at the electrode. Adsorption rates are derived for the plane electrode with control by semi-infinite linear diffusion, the streaming mercury electrode, and electrodes in stirred solution. Adsorption at the dropping mercury electrode is also considered briefly. To simplify the treatment it is assumed either (a) that the concentration of adsorbate is so low as to allow linearization of the isotherm, or (b) that the concentration of adsorbate is so large as to correspond to full coverage. In the range of concentrations in which the isotherm can be linearized, adsorption with diffusion control is a slow process and the equilibrium surface concentration is reached only after a long time (perhaps 30 min). This conclusion is verified experimentally by differential capacity measurements for the adsorption of *n*-hexyl alcohol on a hanging mercury drop in 1*M* potassium nitrate. Conversely, the streaming mercury electrode is essentially free of adsorbate.

Implications are discussed for double layer capacity measurements, electrocapillary curves studies, electrochemical kinetics, and polarography. Maxima and minima and other features of current – time curves during drop life in polarographic reductions in presence of an adsorbable species are accounted for and the dependence of limiting currents on the head of mercury is interpreted. Experimental results are given for the reduction of Cu(II) in 0.5*M* sodium citrate in presence of quinoline.

Experimental methods are discussed, and a simple and accurate bridge for differential capacity measurements without isolation transformer is described.

PART II

The effects of adsorption of non-reducible (non-oxidizable) foreign substances on kinetic parameters for electrode reactions and limiting currents are discussed. The effect of a decrease in effective area and the variations of kinetic parameters (the rate constant k_s at the standard potential and the transfer coefficient) resulting from adsorption can be separated when electrode coverages are determined. Coverages are obtained from measurements of the double layer differential capacity in the absence of the reducible (oxidizable) species. Application is made to the system Ti(IV)/Ti(III) in tartaric medium in presence of *n*-amyl alcohol, cyclohexanol, or thymol. The rate constant k_s is essentially independent of coverage ($\Theta < 0.4$) for the first two substances and decreases markedly for thymol.

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[1] P. DELAHAY AND I. TRACHTENBERG, *J. Am. Chem. Soc.*, 79 (1957) 2355, and another paper in the press.

The effect of adsorption on limiting currents is studied by polarography, electrode coverages during drop life being determined from measurements of the double layer differential capacity. Variations of limiting current with coverage at the end of drop life are studied for several systems. The interpretation of complete waves which are complicated by adsorption of a foreign substance is discussed, and application is made to the cadmium wave in presence of *n*-hexyl alcohol.

Experimental methods are discussed in some detail, and an extrapolation method for minimization of contamination effects is discussed. It is recommended that the dropping mercury (or amalgam) electrode be used in kinetic studies rather than the stationary hanging mercury (or amalgam) drop. Values of k_s obtained with both electrodes are given for the $Cd^{++}/Cd(Hg)$ system at 0°.

DISCUSSION

Prof. H. A. LAITINEN (Urbana):

We have used double layer capacity measurements to measure adsorption as a function of time during the life of slowly forming mercury drops. For many substances that are not extremely surface active, so that the solution concentration is 1 to 10 m*M*, the double layer capacity per unit area is essentially constant during the time interval of 5 to 15 sec of drop life. It appears, therefore, that adsorption equilibrium has essentially been attained during the later portions of drop life.

Prof. P. DELAHAY:

We have also used a similar method of following the differential capacity during drop life. I would agree that one can achieve conditions for which adsorption equilibrium with respect to bulk concentration is practically reached (high enough concentration and long drop time). But this is quite often not the case (drop time of 3-4 sec in polarography).

Mr. G. C. WHITNACK (China Lake, U.S.A.):

In determination of nitrate esters in presence of phthalate esters we have observed considerable dropping of current height of nitrate ester wave before start of phthalate ester wave. Is this due to an adsorption process occurring at the DME?

Prof. P. DELAHAY:

It might well be, but I would hesitate to comment any further on this point because more information would be required. You probably have quite a complicated situation. Perhaps we can discuss the matter later?

Prof. DR. H. FISCHER (Ettingen):

Ich möchte hinzufügen, dass es Fälle geben kann, in denen nicht allein der Blockierungseffekt den Grenzstrom verringert, sondern eine Veränderung des Diffusionsfilmes durch Sekundärreaktion des Inhibitors. Dies ist z.B. bei der Abscheidung von Wasserstoff an einer festen Elektrode (Fe) der Fall, wenn der Inhibitor sich spaltet in eine schwerlösliche Verbindung und ein Proton ($RNH^+ \rightarrow [RN] + H^+$). Dies beobachtet man z.B. bei den Kationen von heterozyklischen Aminen (Acridin). Offentlich bildet sich eine diffusionshindernde Barriere aus.

Prof. P. DELAHAY:

The case of the hydrogen electrode is complicated, and I shall attempt to answer your question only in the case of an ideally smooth electrode. Then, diffusion toward the electrode (partially covered with an adsorbed substance) is little affected by adsorption because the size of "the holes" in the film is very small in comparison with the diffusion layer thickness. Of course, there is no diffusion where there is complete blocking.

Prof. B. BREYER (Sydney):

The importance of the chemical nature of the film adsorbed at the interface, which has been mentioned by Prof. DELAHAY, seems to me to play a major part in the type of processes discussed. Thus it must be kept in mind that complex formation between the dischargeable ion and the adsorbed film might occur (*cf. e.g.* HEYROVSKÝ AND MATYAS, 1941). The fact that Tl^+ ion is little influenced by the presence of an adsorbed film at the electrode solution interface could then be partly explained by the notoriously low co-ordination tendency of that ion.

Prof. P. Delahay:

The difficulty involved in the "blocking" of the limiting current for thallium is due, I think, to the small *size* of this ion (large diffusion coefficient of Tl^+ in comparison with other ions). Of course, complex ions can be relatively very bulky and this enhances "blocking".

Prof. E. Lange (Erlangen):

I agree with Prof. Delahay that it is very important to investigate the connections between the adsorption and electrode reaction.

This is easy for a *steady* state, *e.g.*, each heterogeneous reaction between two phases that is accompanied by a transfer of ions or electrons, *i.e.* of electrical charges, from one phase to the other. In such a case, the Galvani tension does not change and the transfer between the two phases must be compensated by a corresponding transfer of charges within the phases.

But in the *non-steady* state, also, an adsorption process may behave as an "electrode reaction"; for instance, even an adsorption of a dipole molecule may cause a "transfer of charge" accompanied by a corresponding change of the Galvani tension. In this manner, it seems to me that for the *non-steady* state it is necessary to define precisely what one means by "electrode reaction".

Prof. P. Delahay:

I entirely agree with Prof. Lange about the necessity of clear definitions. I think that the fact that a steady state with respect to *diffusion* of the reductible or oxidizable substance has not been reached is not too serious because this scarcely affects the Galvani potential (large excess of supporting electrolyte).

Variations in the amount of adsorbed organic substances indeed affect the Galvani potential (dipole orientation), but this effect is included in the dependence of the rate constant k_s (at the standard potential) on the electrode coverage.

Prof. N. Tanaka (Sendai, Japan):

I am very grateful to Prof. Delahay for his beautiful work on adsorption kinetics. I should like to make one comment in connection with the rotated dropping mercury electrode. The relation between log i and log t on the current – time curve was found to be 0.5 only in the absence of the surface-active substance. In the presence of surface-active substance, the slope of log i *vs.* log t changed at a certain point of the current – time curve. This can be explained when the slow adsorption of the surface-active substance on the surface of the electrode is taken into consideration.

Prof. P. Delahay:

Even for stirred solutions, adsorption equilibrium is not reached very rapidly. A simple calculation based on a model of the Nernst diffusion layer shows that perhaps 1-5 sec are required. Your conclusion is, therefore, quite correct.

Prof. W. Kemula (Warsaw):

We have recently published that, in several cases, the addition of extremely small concentrations of organic surface-active substances provokes at first a *rise* of the diffusion current, this current then being suppressed by additional quantities of the substance.

NEW TECHNIQUES IN RADIOCHEMICAL DETERMINATIONS USING POLAROGRAPHIC METHODS

by

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INTRODUCTION

In almost all radiochemical determinations not only the activity of the radioisotope must be determined after its separation from other activities, but also the per cent of added inactive carrier present when the radioactivity is measured. This quantity is a measure of the yield of the radioactive isotope that has been recovered from the initial aliquot. Radiochemical yields of about 80% are common, thus implying that the various steps in the procedure need not be quantitative, decontamination from other radioactive elements being the first requirement.

Processes that take place polarographically offer excellent methods for decontamination, although the yields of the total separations are extremely low. If the radioactive isotope is polarographically reduced to the zero oxidation state, the resulting metal forms a dilute amalgam with the mercury drop which can be removed from the solution and the amount of radioactivity measured. Since the amount of activity collected will be constant for each drop of mercury at a given potential and a given drop time, a measure of the quantity of the radioisotope that is present may be found by counting, *e.g.*, in a NaI(Tl) crystal well. The necessary amount of activity is separated by collecting enough drops from a solution of known volume.

The requirements for the quantitative polarographic determination of an isotope is that it be polarographically reduced or oxidized to the zero oxidation state and amalgamate with the mercury, and in a mixture of isotopes it will be the only element reduced at the given potential. Since such small quantities are involved, especially in carrier-free solutions, extremely dilute amalgams are likely to be formed with most metals. The activity of a radioactive isotope on a mercury drop should be independent of the amount of stable isotopes of that element in solution. The concentration gradient around a drop of mercury above the reduction potential of the element being determined is the same for the active as well as the stable isotopes of that element. Therefore, this method should serve also as a good qualitative method of analysis for a mixture of radioactive isotopes because it does not require the forehand knowledge to add an inactive carrier to the unknown solution as it does in most other radiochemical procedures. A γ ray spectrometer may be used to determine which activities from a mixture of activities are associated with the mercury drops.

APPARATUS AND REAGENTS

Polarographic data were obtained from a Leeds and Northrup Electro-Chemograph Type E. The polarographic cell shown in Fig. 1 is used as follows. Mercury is placed in the side arm containing the platinum electrode and the cell with the stopcock closed is filled with carbon tetrachloride to just below the mercury pool electrode. If the mercury pool electrode cannot be used, a small saturated calomel electrode may be inserted into the solution. This electrode can make contact with the solution through a small piece of glass tubing filled with a saturated potassium chloride agar gel with a sintered-glass plug separating the solution from the agar gel. The active solution is placed above the carbon tetrachloride and in contact with the electrode. The dropping mercury capillary is placed in the solution. The purpose of the large volume of carbon tetrachloride in the other compartment is to keep the solution – carbon tetrachloride interface at a constant height when the mercury drops fall through the solution and are removed by turning the stopcock. The size of the cell can be either large or small depending on the volume of solution to be analyzed. The distance which the mercury drops through the carbon tetrachloride can be much longer if the solutions are very radioactive so that the cell compartment may be shielded. 8 mm glass tubing is used and the overall height of the cell is 18 cm. The temperature of the room is considered constant enough at 25°C not to require thermostating the solution. However, this may be done simply, if necessary, by placing a water jacket around the solution compartment. It has not been found necessary to remove dissolved oxygen from the solution although if required in the special cases comparing polarograms with curves of activity *vs.* E_{de} for carrier and carrier-free solutions, this may be done by inserting a small tube into the solution and bubbling through oxygen-free nitrogen gas.

All isotopes were obtained from Oak Ridge National Laboratories (see Table I).

TABLE I

DESCRIPTION OF ALL ISOTOPES USED

Isotope	*Specific activity*	*Purity*	*Half-life*	*Chemical form of soln.*
^{95}Zr-^{95}Nb	CF	97%	65 days	oxalate complex in 0.5% oxalic acid
^{60}Co	10^4 mc/g Co	99%	5.27 yrs	$CoCl_2$ in 1*N* HCl
Mixed fission products	—	—	—	nitrates in 1-6*N* HNO_3
^{106}Ru-^{106}Rh	CF	99% no Ru^{103}	1 yr	$RuCl_3$ in 6*N* HCl

PROCEDURE

The carbon tetrachloride and either the mercury for the mercury pool electrode or a small saturated calomel electrode are placed in the cell shown in Fig. 1. The supporting electrolyte solution (usually 1 ml) is added on top of the carbon tetrachloride and in contact with the stationary electrode. A few lambda of the radioactive isotope are added to the supporting electrolyte solution and stirred with the micropipette. The mercury drops (drop time is 5 sec unless otherwise stated) from the dropping mercury electrode are allowed to fall through the carbon tetrachloride to the top of the stopcock and are collected in a 15 × 125 mm test tube, either one at a time or else a predetermined number, by opening the stopcock. Sometimes a small amount of active solution will adhere to the mercury drop as it falls through the carbon tetrachloride. The drops are therefore allowed to fall into a test tube containing about 1/2

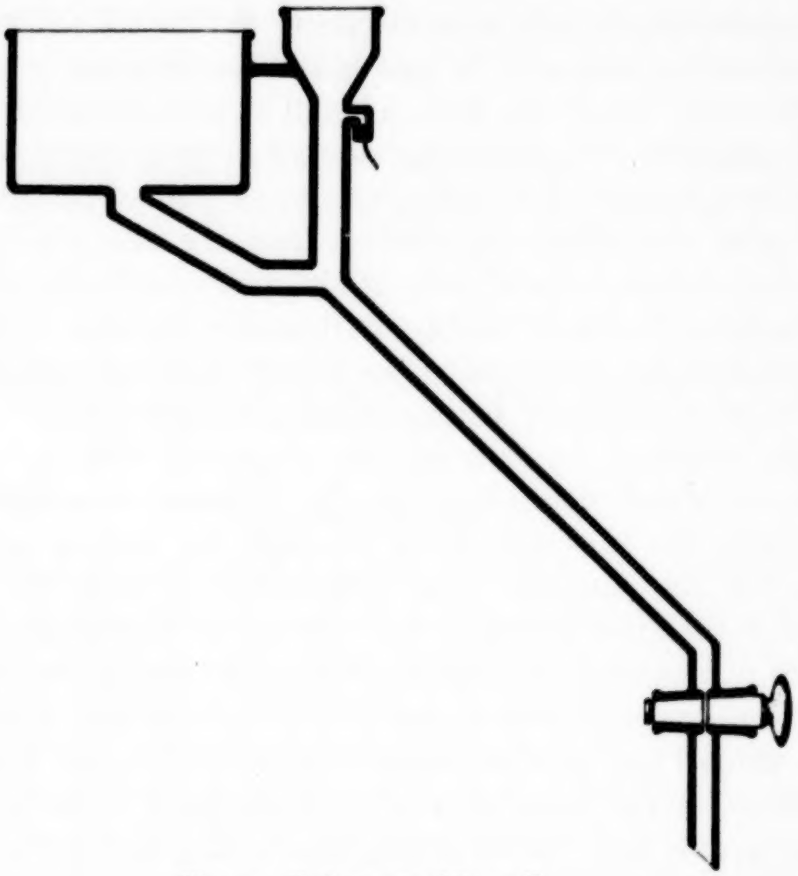

Fig. 1. Polarographic cell.

ml of carbon tetrachloride. The carbon tetrachloride is sucked away from the mercury drop with a small piece of plastic tubing connected to a vacuum. The mercury drop is then poured into a clean test tube. This last step is necessary because of the chance of some of the active liquid adhering to the walls of the first tube. The mercury collected either is measured for γ activity in a NaI(Tl) crystal well γ counter, or a γ spectrum is taken with a γ spectrometer. From these measurements the disintegration rate of the radio-isotope may be found from the known efficiency of the γ counter for that radio-isotope, or the γ energy, and hence the isotope, may be found from the γ energy(s) obtained. β energies and disintegration rates may also be found by dissolving the activity from the mercury drop with a small amount of dilute hydrochloric acid, placing this solution on a thin plastic film, evaporating to dryness, and β counting it in either an end-on β counter or a 4-π β counter. All the activity of the isotopes used here may be removed from the mercury drop with dilute hydrochloric acid.

RESULTS AND DISCUSSION

The similarity of the polarographic reduction of tracer and carrier solutions

Approximately 50 λ of the ^{60}Co solution containing $3.10 \cdot 10^8$ d.p.m. with inactive cobalt carrier present (Table I) was added to 2 ml of water. Table II compares the activity of the cobalt amalgam collected at different potentials with the microamps of current produced in the polarographic reduction of the cobalt carrier. The measure of the time is in arbitrary units corresponding to divisions on the polarographic paper which moved at a constant rate. This made it convenient to turn on the chart drive at a given potential at the start of a run and to turn off the chart drive at any convenient time when the last drop was collected.

TABLE II

COMPARISON OF CURRENT *vs.* E_{de} OF INACTIVE COBALT WITH GAMMA ACTIVITY *vs.* E_{de} FOR COBALT-60

Run	E_{de}	Time (arbitrary units)	c.p.m.	I_d	$T \times I_d$	c.p.m./$T \times I_d$
1	—1.4	7.90	2978	0	0	
2	—1.5	7.17	22912	8.5	61	376
3	—1.6	7.77	82688	30	233	355
4	—1.7	6.83	96640	36	246	393
5	—1.9	5.3 1.13	306176	120 83	729	420

The ratio of the c.p.m. of the ^{60}Co amalgamated at the given potential to the quantity of current produced at the same potential is listed in the last column of Table II. The approximate constancy of this ratio indicates that the polarographic reduction of the extremely dilute ^{60}Co and the carrier are the same. The apparent irregularity of the polarogram is probably due to a visible layer of precipitate on the surface of the mercury pool at about —1.7 V.

Fig. 2 presents further evidence that the tracer ^{60}Co underwent the same type of polarographic reduction as the inactive carrier cobalt. This curve was produced by taking a polarogram of the cobalt solution, collecting each drop as it fell, and γ counting each drop. The c.p.m. obtained for the individual drops are shown in the figure.

Conventional radiochemical analyses require the presence of isotopic carriers to carry out the various chemical manipulations. Thus, in conventional radiochemistry it is necessary — or, at the very least, highly desirable — that prior knowledge of the radionuclide composition of the sample be available. The results obtained by use of the polarographic technique with ^{60}Co suggest that it is not necessary to include isotopic carriers to conduct the analyses. This conclusion is supported by similar results with carrier free solutions.

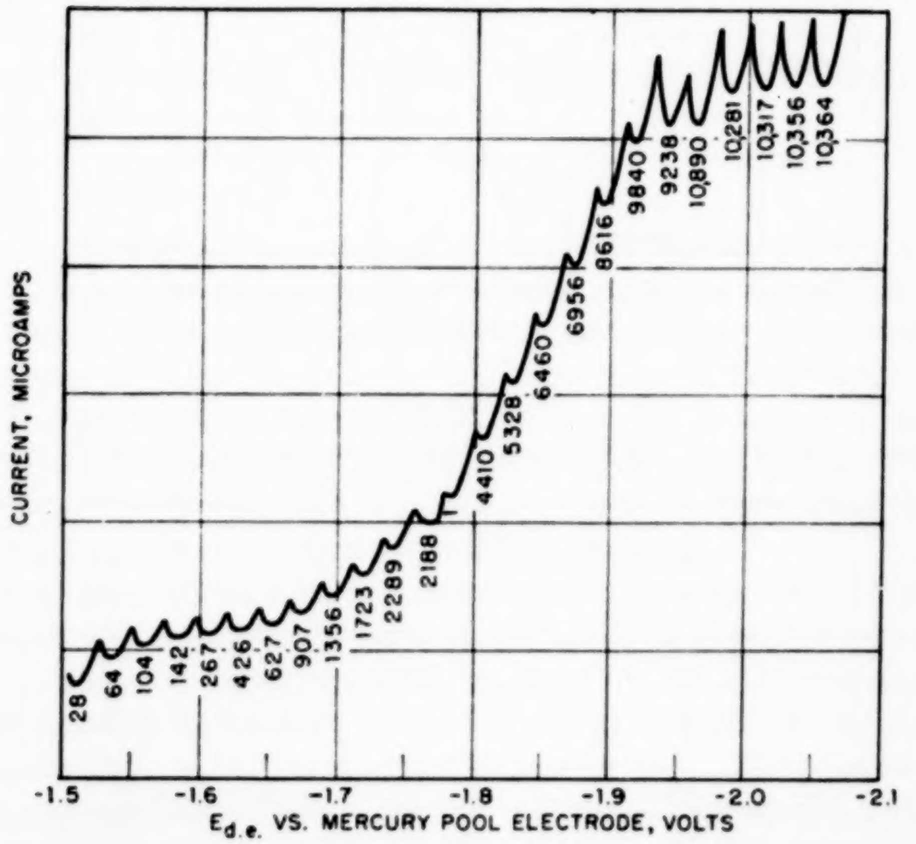

Fig. 2. Cobalt-60.

The polarographic separation of radionuclides in absence of isotopic tracer

Zirconium-95 – niobium-95

The first separation of radionuclides by the subject technique was carried out with zirconium-95 and its daughter niobium-95. LAUBENGAGER AND EATON[1] found a half-wave potential of —1.65 V *vs.* S.C.E. for a zirconyl solution in 0.1N potassium chloride and concluded that the reduction of the zirconyl ion was to the metallic state. The polarographic reduction of niobium to the metal has not been reported and is unlikely.

Twenty-five λ of carrier-free equilibrium mixture of zirconium-95, niobium-95 having a total disintegration rate of $2.41 \cdot 10^8$ d.p.m. was placed in exactly 1 ml of 0.1N KCl. A voltage – activity curve of this solution was obtained at a drop time of five seconds. The results obtained are shown in Fig. 3 and in Table III. Each point represents the activity amalgamated at a given voltage for three minutes. The decay of the separated zirconium followed closely that which would be computed as the niobium grew in from a zero initial amount.

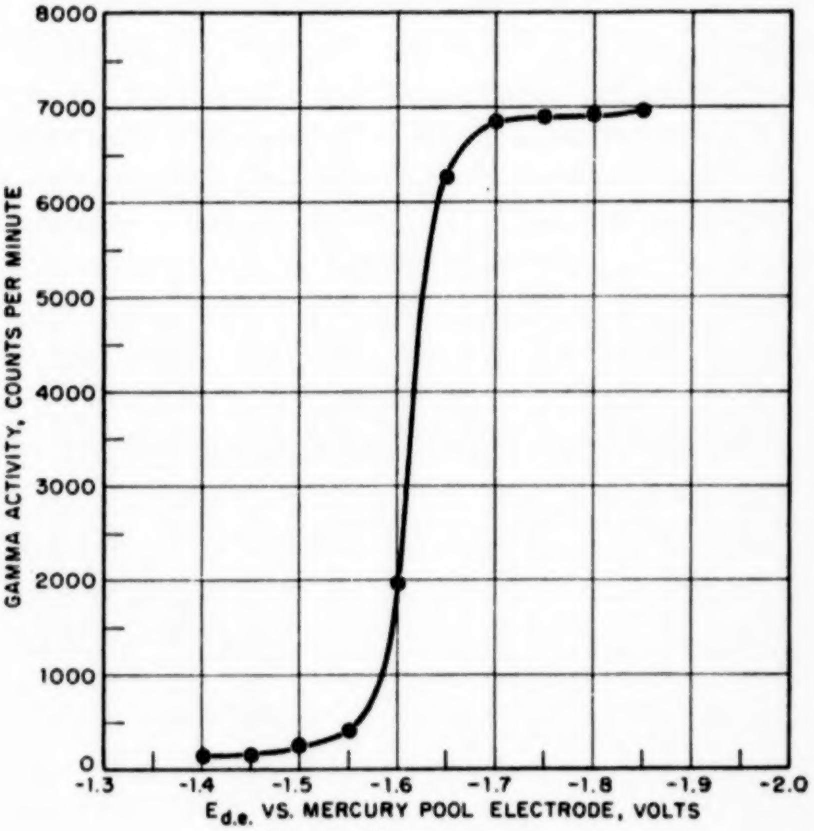

Fig. 3. Zirconium-95.

TABLE III

GAMMA ACTIVITY OF ZIRCONIUM-95 COLLECTED AT VARIOUS POTENTIALS

Run	E_{de} *vs. mercury pool electrode*	*Gamma activity (c.p.m.)*
1	—1.40	134
2	—1.45	140
3	—1.50	260
4	—1.55	400
5	—1.60	1917
6	—1.65	6275
7	—1.70	6872
8	—1.75	6886
9	—1.80	6907
10	—1.85	6953

Three additional experiments with the Zr–Nb pair were carried out. A small amount of zirconium hydroxide was added to the above zirconium-95–niobium-95 solution so that a polarogram was formed with a diffusion current height of about 2 μamp. No change was noticed in the amount of zirconium-95 that was collected at any voltage. Drops collected for a 3-min interval as above gave γ counts of 52 c.p.m. at —1.3 V and 6872 c.p.m. at —1.7 V *vs.* the mercury pool electrode.

A new solution of zirconium-95–niobium-95 prepared in the same way as above except that twice the activity of zirconium-95 was added. The values obtained at —1.3 V and —1.7 V were 78 c.p.m. and 13,693 c.p.m., respectively

These results indicate that zirconium is quickly and completely separated from niobium by this procedure. Further, the amount of inactive zirconium present makes no noticeable difference in the amount of zirconium amalgamated and hence the forehand knowledge that zirconium is present is not required. This method of separation is quantitative because the activity of the zirconium amalgams are proportional to the amount of zirconium-95 in solution.

To the last solution used above was added cerium-144, ruthenium-106, cesium-137, beryllium-7, and cobalt-60 activities. Under the same conditions as above the activities obtained at —1.3 V and —1.7 V were 6238 c.p.m. and 20,192 c.p.m., respectively. The difference of the two values is very close to that obtained for the pure zirconium-95–niobium-95 solution.

The results of these experiments indicate the following: (a) Zr was quickly and completely separated from Nb; (b) the amount of inactive Zr present made no difference on the amount of ^{95}Zr amalgamated; (c) the activity of the zirconium amalgams was proportional to the amount of ^{95}Zr in solution and hence the method of separation is quantitative; and (d) other radionuclides may be present in the solution provided they are not reduced at the same potential and the method will remain quantitative.

Calculations show that 510 d.p.m. per 5-sec drop of zirconium-95 was removed from a solution containing $2.35 \cdot 10^8$ d.p.m. per ml of zirconium-95–niobium-95. Therefore, $6.88 \cdot 10^{-4}$ % of the zirconium-95 was removed per 5-sec drop per ml. This corresponds to $7.0 \cdot 10^{10}$ zirconium-95 atoms per 5-sec drop.

Ruthenium-106 – rhodium-106

Since an approximately constant number of ions in a given solution are reduced to the zero oxidation state on each mercury drop in any reduction of this kind, the half-life of the radionuclide involved will determine the sensitivity of the measurement. In general, the shorter the half-life of the isotope being reduced, the greater the sensitivity of detection. Ruthenium-106 with a half-life of one year decays to rhodium-106 with a half-life of 30 sec. Hence, in the polarographic separation of rhodium-106 from ruthenium-106 the sensitivity should be good, and, moreover, a separation of this sort should permit an excellent evaluation of the separation efficiency.

The polarographic reduction of ruthenium to the zero oxidation state has not been reported in the literature. The polarographic reduction of +3 rhodium to the zero oxidation state on the other hand has been reported by WILLIS[2] in a 0.9M potassium thiocyanate solution. A half-wave potential of —0.39 V *vs.* S.C.E. for rhodium under these conditions was too positive, so that WILLIS proposed the reduction did not go from +3 to +1 (it was found that $n = 2$), but that the reduction of +3 to +2 occurs at a potential more positive than that at which the anodic dissolution current occurs, and the wave found at —0.39 V is the reduction of +2 to 0. If it is true, as **Willis** proposes, that rhodium is reduced to the zero oxidation state, a quick method of separation of the rhodium-106 from the ruthenium-106 is possible.

600 λ of ruthenium-106 - rhodium-106 was evaporated to dryness and taken up to 500 λ with 1 *M* potassium thiocyanate supporting electrolyte. The total activity was $1.64 \cdot 10^9$ d.p.m. The mercury drops were collected at various potentials, and it was found that no rhodium-106 was separated below —0.2 V while about a constant amount was separated at any voltage more negative than —0.7 V *vs.* mercury pool electrode (see Table IV).

TABLE IV

HALF-LIFE OF RHODIUM-106

Run	E_{de} *vs. mercury pool electrode (volts)*	*No. of drops*	*No. of points plotted*	*Half-life (sec)*
1	—2.0	5	13	29.2
2	—0.6	5	12	29.2
3	—1.0	5	13	28.8
4	—0.8	1	13	30.0
5	—0.8	1-1/2 min	14	28.7
6	—0.8	1	14	30.0
7	—0.8	1	13	30.2
8	—0.8	1	14	28.4

The time required from the formation of one drop to the beginning of the counting of this drop was less than thirty seconds. Ten second counts were taken of the rhodium-106 and approximately 13 counts were taken before the rhodium decayed out. The initial 10-sec count was usually about 50,000 counts which decayed to a constant count of about 2000 counts per 10 sec. It was calculated that about a 2% impurity of ruthenium-106 was in the rhodium-106 at the time of the first count. It was not found necessary to apply the correction of **Sargent** *et al.*[3] to account for the decay of the rhodium-106 during the 10-sec count.

The value of the half-life obtained from eight decay curves of rhodium-106 is 29.3 ± 0.65 sec.* This compares with a value of 40 sec by **Seelmann-Eggebert**[4] and 30 sec by **Glendenin**[5].

Results with fission products

1500 λ of ORNL fission products made 1 *N* with HCl were analyzed in the same manner as were the individual isotopes listed above. These fission products were about six months old and contained mostly gamma emitting isotopes of cerium-144 - praseodymium-144, zirconium-95 - niobium-95, and ruthenium-106 - rhodium-106 along with smaller amounts of many other isotopes. The activity of this solution was about 50 μc (gross β count). Each run in Table V represents the amount of activity found on mercury drops collected for five min. As can be seen, two activities appear to be reduced to the zero oxidation state. One is completely reduced at —0.1 V *vs.* mercury pool electrode and the other at —1.9 V. A γ spectrum of both of these substances showed only the ruthenium-106 - ruthenium-103 peak along with the 40 keV rhodium-103 peak which would grow in from the ruthenium-103 with its 57 min half-life. No other de-

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* The half-life value given here along with other short half-life determinations will be submitted in greater detail to *The Physical Review*.

TABLE V

GAMMA ACTIVITY OF FISSION PRODUCTS COLLECTED AT VARIOUS POTENTIALS

E_{de} *vs. mercury pool electrode (volts)*	*Counts/5 min*	*Counts/5 min (diluted 1/2)*	*Counts/5 min (diluted 1/4)*	*Counts/5 min (diluted 1/8)*
+0.2	659			
+0.1	680			
0.0	726			
—0.1	3107	1532	771	390
—0.2	3092			
—0.3	3111			
—0.4	3211			
—0.5	3086			
—0.6	3089			
—0.7	3117			
—0.8	3099			
—0.9	3172			
—1.0	3107			
—1.1	3119			
—1.2	3186			
—1.3	3072			
—1.4	3141			
—1.5	3162			
—1.6	3242			
—1.7	3200			
—1.8	5818			
—1.9	8196	4081	2005	1047
—2.0	8202			
—2.1	8171			

tectable γ photopeaks could be seen although both the zirconium-95 - niobium-95 and cerium-144 peaks were much larger than the ruthenium-106 - ruthenium-103 peak in the original fission product spectrum.

The concentration of the solution was diluted to half with the supporting electrolyte. The activity on the mercury was half what it was before at —0.1 V and —1.9 V *vs.* mercury pool electrode. The γ spectrum showed the ruthenium peak at only about half what it originally was. The solution was diluted two times more by half and again the activity of the mercury drops was half what it was.

Using various other supporting electrolytes it is felt that other fission products may be reduced and analyzed by this method. Work being carried out at this laboratory includes this type of analysis for the activity separated from deuteron bombarded steel samples. Also, procedures for beryllium-7, cesium-137, tin-113 - indium-113 m, barium-133, and zinc-65 have been developed. At the same time more basic work of the underlying principles of this type of analysis and of its further application are being investigated.

CONCLUSIONS

The results obtained from the experiments described here indicate the polarographic technique developed has a very large potential use to the chemist by not only enabling him to carry out quick accurate analyses and separation of radionuclides, but also to learn more basic electrochemistry of dilute solutions and of electrode reactions. Now that the experimental techniques of collecting and measuring the activity polarographically deposited on the mercury drops has been successfully accomplished many applications to various other fields of chemical research are possible.

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SUMMARY

This work was undertaken as part of a research program on the development of new radiochemical procedures. The techniques used are those of standard polarographic practices. Radioisotopes that can be polarographically reduced to the zero oxidation state amalgamate with the mercury, are removed from the solution, and the radioactivity determined. Reproducible curves of activity *vs.* E_{de} are found to be in every way analogous to polarograms obtained under the same experimental condition. The requirements necessary for any radio-isotope to be determined quantitatively by this method are that the radio-isotope be polarographically reduced to the zero oxidation state and that no other radio-isotope be polarographically reduced at the same potential. This type of analysis has been successfully applied to several radio-isotopes and mixtures of radioisotopes.

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DISCUSSION

Prof. R. L. Pecsok (Los Angeles):

What was the order of magnitude of the concentrations of solutions polarographed? Were the polarographic currents involved far below the range of measurement by ordinary techniques?

Dr. D. L. Love:

The order of magnitude of all the radioactive substances described here were about 100 μc. This represents a number of atoms that would form a solution much less concentrated than the most dilute solutions analyzed by normal polarographic techniques. A most important application of this method of analysis is the radioactive quantitative and qualitative determination of extremely radioactively "hot" solutions since there is only $10^{-4}\%$ of the radioactive substance removed for each five second Hg-drop.

Prof. B. Breyer (Sydney):

It has to be kept in mind that after the Hg-drop is detached from the capillary, it finds itself at a different potential than before detachment. Hence dissolution of metal from the amalgam might occur while the drop is falling through the solution.

Dr. D. L. Love:

The Hg-drop forms just above the aqueous–CCl_4 interface and the time after detachment that it spends in the aqueous phase must be a very small fraction of a second before it reaches the CCl_4. For regular analytical determinations this is of no concern as long as the drop time and distance to the aqueous–CCl_4 interface are constant; however, it might be of concern in an absolute determination. I believe that if dissolution does occur, the straight-lined relationship of activity *versus* the potential of the dropping electrode would not have been obtained. If this is the case or not, it is certainly something to be considered in any future absolute determinations.

ANODIC STRIPPING VOLTAMMETRY WITH MERCURY ELECTRODE POTENTIAL-STEP AND CURRENT-STEP METHODS

by

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Since this investigation has been published elsewhere[1], only a summary will be given here for reference in the discussion section.

An amalgam-forming metal is deposited on a stationary mercury electrode and then is anodically oxidized. Anodic stripping is carried out either by sudden switching of potential (potential-step method) or by passing a constant current through the cell (current-step method). A theoretical analysis is devoloped for both methods for conditions of semi-infinite linear diffusion. The following derivations are given: equations for current - time, current - potential, and potential - time curves; diffusion current and transition time for the stripping process; sensitivity gain. Detailed experimental results are discussed for the anodic stripping of cadmium from a hanging mercury drop, and theory and experiment are compared. Sensitivity gains with respect to voltammetry with stirred solution can be larger than 100. Application to concentrations as low as 10^{-7}-$10^{-9}M$ appears feasible. These two methods are compared with anodic stripping at continuously varying potential (NIKELLY AND COOKE).

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DISCUSSION

Prof. N. TANAKA (Sendai):

(1) What is the difference of this method and the method proposed by Dr. HICKLING?

(2) How can this method be applied when two substances are present in the solution?

Prof. P. DELAHAY:

(1) If I recall correctly HICKLING in his work recently published [*Anal. Chim. Acta*, 14 (1956) 297] carries out the anodic oxidation with a stirred amalgam. I would say that method is quite different from that of HICKLING.

(2) The situation is similar to that in polarography. Both metals are deposited, and the potential first switched at a value at which only the nobler metal is oxidized. A second current - time curve is recorded at a potential at which both metals are oxidized. The concentration of the less noble metal is obtained by difference.

Prof. H. A. LAITINEN (Urbana):

(1) What are the relative sensitivity limits of the potential step and current step methods?

(2) Would Prof. DELAHAY care to comment on the application of these methods with solid microelectrodes? Here no diffusion can occur within the electrode and diffusion in the solution is ill-defined.

Prof. P. DELAHAY:

(1) Sensitivities are quite comparable although the potential-step method is more sensitive than the current-step method.

(2) These methods can be applied to solid electrodes but a coulometric determination must then be made. Direct evaluation of the concentration from the current-time caracteristics (potential – time curves in the current-step method) is only possible when less than a monolayer is involved (or perhaps a few layers for a non-uniform deposit). See the recent work of NICHOLSON published in *J. Am. Chem. Soc.*

Dr. H. GERISCHER (Stuttgart):

(1) Wenn ich Sie recht verstanden habe, beruht die grosse Empfindlichkeit der Methode darauf, dass eine elektrolitische Trennung und Anerkennung der Untersuchungssubstanz in dem kleinen Hg-Tropfen erfolgt.

(2) Wie wird die Auswertung des anodischen Stromstosses vorgenommen; durch einfache graphische Integration?

(3) Glauben Sie nicht, dass die starke Konvektion in der Lösung auch eine Konvektion im Amalgam zur Folge hat, was zu einem weitgehenden Konzentrationsausgleich im Amalgam führen sollte wenn τ relativ gross ist?

Prof. P. DELAHAY:

(1) The gain in sensitivity is indeed due to the extraction of the metal from the solution into a thin layer of mercury. The metal is deposited into mercury at a rate larger than that at which it can diffuse away.

(2) There was no current integration but only direct measurement on the recorded current-time curve.

(3) Convection obviously interferes but reproducible conditions can be achieved in analytical applications.

Dr. MECHELYNCK (Mol, Belgique):

Dans le cas où les temps d'électrolyse sont longs, le gain expérimental est supérieur au gain théorique. Je pense qu'au point de vue analytique c'est un avantage, puisque ce phénomène, qui est dû à la sphéricité de l'électrode, est parfaitement reproductible si les électrolyses sont effectuées pendant des temps identiques. Est-ce effectivement le cas?

Prof. P. DELAHAY:

Tout à fait d'accord. On est toutefois limité par la solubilité du métal dans le mercure.

Prof. W. KEMULA (Warsaw):

Which substances have you studied? Have you met difficulties with purification of basic electrolytes?

Prof. P. DELAHAY:

Our study was limited to the development of some fundamental ideas and their verification and not with the details of application. We studied primarily cadmium. I might add that other metals were studied by NIKELLY AND COOKE in the work they reported at the Lisbon IUPAC meeting (see recent publication in *Anal. Chem.*).

The purification of the supporting electrolyte is a serious problem. Another problem is the necessity of equilibrating the solution with its container. However, these difficulties are often common to many trace analysis methods.

FACTORS TO BE CONSIDERED IN QUANTITATIVE POLAROGRAPHY WITH THE ROTATED DROPPING MERCURY ELECTRODE*

by

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Since the recent development of the rotated dropping mercury electrode (RDME) in this laboratory[1] for the purpose of improving the sensitivity of polarographic determinations, this electrode has found a potentiality not only in trace determinations but also in various theoretical studies. Maxima of the first kind (ordinary polarographic maxima) have not been observed at the RDME, but maxima of the second kind are very pronounced at this electrode. Quite generally, in quantitative polarography with the RDME it is necessary to add a suitable maximum suppressor. Such a suppressor is adsorbed at the interface mercury – water, and it is desirable that it remain adsorbed in the entire potential region where the RDME can be applied. A desorption of the suppressor is accompanied by an increasing limiting current of the electroactive species in the solution. This desorption current allows a characterization of the suppressor and under suitable conditions an estimation of its concentration. At a given rate of rotation of the RDME the dependence of the limiting current upon the drop time, flow of mercury and diffusion coefficient of the electroactive species is different from that of the diffusion current at the conventional dropping mercury electrode (DME). The effect of drop time on the limiting current at the RDME is relatively large and this effect must be considered in a quantitative analysis of mixtures of electroactive constituents. In the present paper a review is given of the various factors which affect the limiting current at the RDME.

CONSTRUCTION OF THE ELECTRODE

Three suitable types of RDME are illustrated in Fig. 1. Type C, in which the rotated and unrotated parts are joined through syringe pieces enabling to vary the mercury pressure, is convenient for systematic fundamental studies of the effect of drop time and of rate of mercury flow. Types A and B are more suitable for practical analyses because of simplicity of their assembly. A small decrease of mercury pressure resulting from the consumption of mercury during several experiments is of no practical consequence because the effect of the height of mercury upon the limiting current at the RDME is very small and quite different from that at the DME (*vide infra*)[2].

A few precautions must be observed in constructing a RDME which functions with a satisfactory reproducibility. (1) The edge at the orifice should be as thin as possible. (2) In types A and C no air bubble should remain in the space between the

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* This investigation was supported by a research grant from the National Science Foundation.

lower end of the capillary and the upper end of the end tube. (3) The diameter of the orifice should not be much greater than 1 mm. (4) The tip must be properly coated with a water-repellent for preventing electrolyte solution from creeping into the glass tubing during electrolysis. A liquid silicone preparation (G.E. Dri Film SC 87 obtained from Central Scientific Co., Chicago) has been found to be suitable. (5) Eccentric rotation should be avoided. If one or more of these conditions are not fulfilled, current oscillations and the drop time tend to become irregular with increasing negative potential.

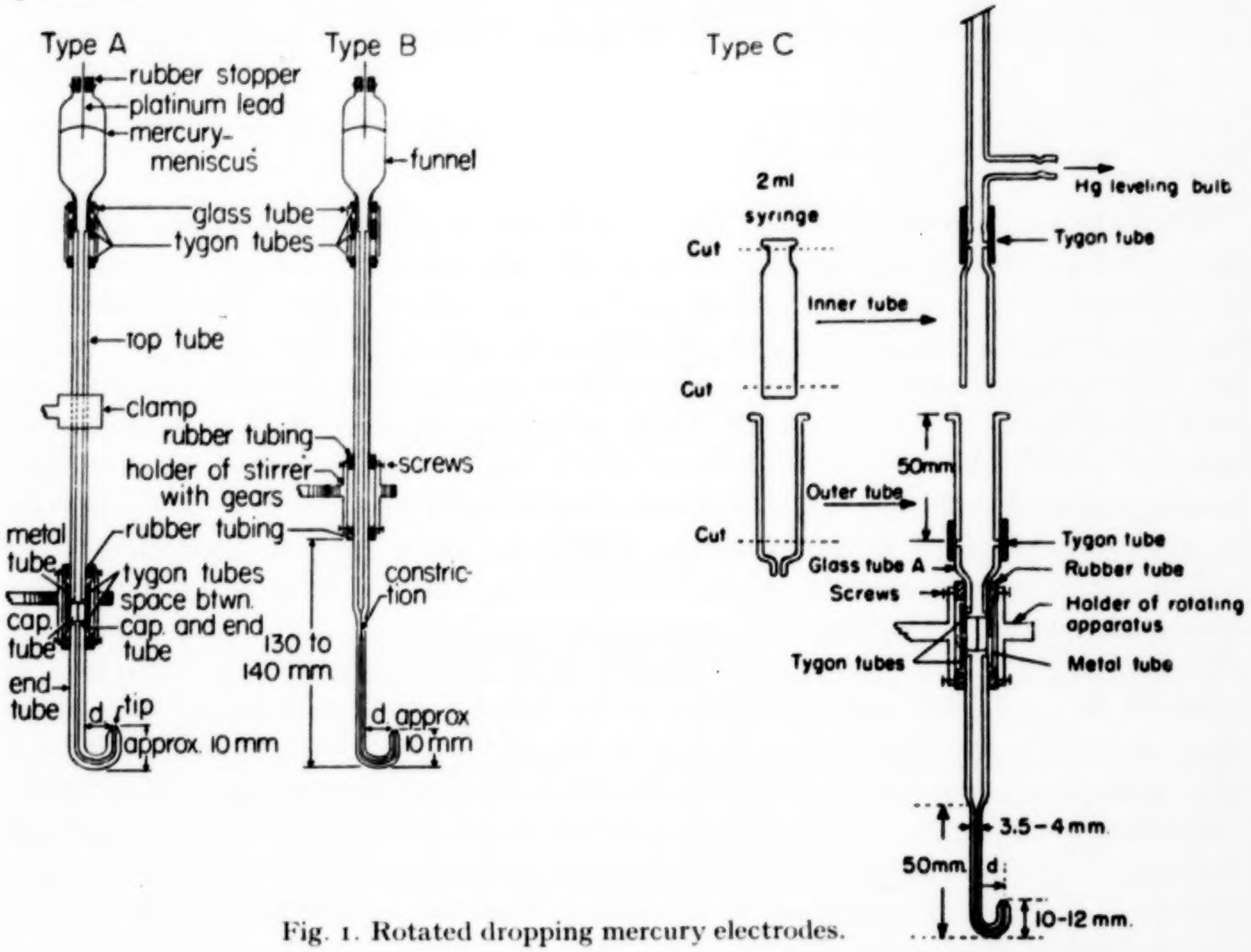
Type A
rubber stopper
platinum lead
mercury-meniscus
glass tube
tygon tubes
top tube
clamp
metal tube
tygon tubes
space btwn. cap. and end tube
cap. tube
end-tube
d
tip
approx. 10 mm
Type B
funnel
rubber tubing
holder of stirrer with gears
screws
rubber tubing
constric-tion
130 to 140 mm
d approx 10 mm
Type C
2 ml syringe
Cut
Cut
Cut
Inner tube
Outer tube
50mm
Hg leveling bulb
Tygon tube
Tygon tube
Rubber tube
Glass tube A
Screws
Holder of rotating apparatus
Tygon tubes
Metal tube
3.5–4 mm
50mm
d
10–12 mm

Fig. 1. Rotated dropping mercury electrodes.

Regularity of the behavior of the RDME can be best checked by plotting log i_1 (the average limiting current) *versus* log t (the drop time) at various potentials using a solution of a suitable metal ion containing a proper surface active substance (*vide infra*). If the electrode is functioning properly, this plot yields a reasonably good straight line with a slope of 0.5 to 1 depending on the size of the orifice. A further description pertaining to this relationship is given in a subsequent section.

CHARACTERISTICS OF THE ELECTRODE

Some current-potential curves of mercurous ions at various concentrations of sodium nitrate are shown in Fig. 2. Curves A to F were obtained in the absence of gelatin, while curve G was obtained in the presence of 0.01% gelatin. Upon addition of gelatin, all of the curves A to F attain the same shape as curve G, and the limiting current decreases to a considerable extent at all potentials. It is clear that the limiting current-potential relation in the absence of surface active substances and the large effect of the addition of such a substance over the entire region of the current -potential curve are strikingly different at the RDME than at the DME.

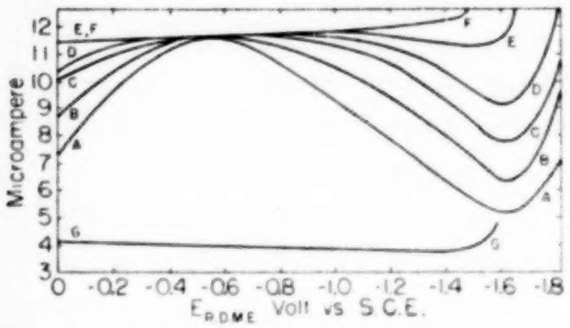

Fig. 2. Current-potential curves of $5 \cdot 10^{-5} M$ Hg_2SO_4 in sodium nitrate solutions of various concentrations in $NaNO_3$ (210 r.p.m., $t = 5.3$ sec, $m = 9.37$ mg/sec, open circuit): A, 0.01; B. 0.05; C, 0.10; D, 0.25; E, 0.50; F, 1.00M $NaNO_3$; G, 1.00M $NaNO_3$ 0.01% gelatin.

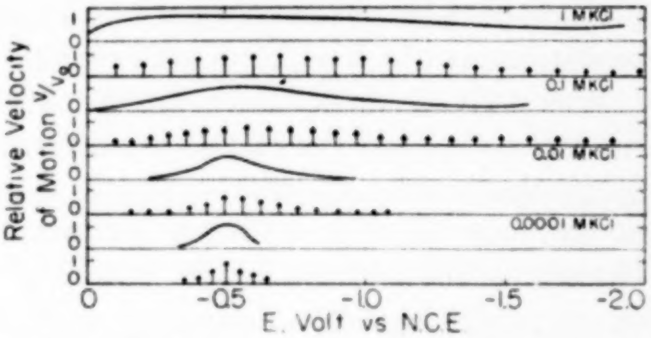

Fig. 3. Relative velocity of motion of potassium chloride around mercury drop. Arrows indicate experimental values, and curves are constructed from calculated values, both obtained by FRUMKIN *et al.*[4] v_0 is velocity at potential of electrocapillary zero, v velocity at any other potential.

Limiting currents in the absence of surface-active substances

One of the marked differences between the RDME and the DME is that the limiting current-potential curve in the absence of capillary active substances at the RDME does not exhibit maxima of the first kind (the ordinary maxima observed at the DME) even when the electrode is not rotated. According to the interfacial tension theory of VON STACKELBERG[3], maxima of the first kind observed at the DME are attributed to a streaming at the mercury-solution interface which arises from differences in surface tension at various parts of the drop surface, when current passes. These differences in surface tension are caused by differences in current densities at different places on the mercury surface; *i.e.*, at the drop neck the current density is less than at other parts of the drop, because of the "screening" by the base of the capillary. It is possible that the design of the RDME probably excludes this screening effect. Further systematic study of the effect of shape, thickness of the wall of the tip and position of the capillary (horizontal, vertical) of the DME on maxima seems desirable.

VON STACKELBERG[3] refers to ANTWEILER's experiments which showed that the flowing of mercury out of the capillary of the DME *into* the growing mercury drop gives rise to a vortex motion within the drop. This vortex motion is transmitted to the solution, resulting in a tangential streaming. FRUMKIN *et al.*[4] showed experimentally and theoretically that this tangential streaming varies with the potential of the mercury and with the ionic strength of the solution. Diagrams illustrating this situation are reproduced in Fig. 3. The streaming velocity is always largest at the potential of the electrocapillary zero, where there is no electrical double layer present at the interface. At other potentials the forces acting on the two sheets of the double layer decrease the mobility of the interface and hinder the streaming. This streaming resulting from the vortex motion inside the mercury drop brings about maxima of the second kind in the current-potential curve at the DME if the drop time is small (less than about 3 sec) and the supporting electrolyte concentration is sufficiently high (greater than about 1M). The striking resemblance at the same ionic strength between curves in Fig. 3 and limiting current-potential curves at the RDME (Fig. 2) indicates that the larger limiting currents at the RDME in the absence of surface-active substances are to be attributed to the streaming at the mercury-solution interface which are responsible for maxima of the second kind. It is apparent that the rotation of the electrode gives rise to an enhanced streaming at the interface even under conditions at which maxima of the second kind are not observed at the DME.

We[2] derived an equation for the average limiting current involving maxima of the second kind at the RDME by assuming that the mercury drop is a perfect sphere expanding from its center outwards symmetrically and that the streaming velocity on and near the drop surface is uniformly equal to U_0 cm/sec. U_0 varies with the ionic strength of the solution and the potential of the mercury. At a given potential and ionic strength, the equation derived at 25°C is

$$i_1 = 230nCD^{1/2}\{m^{2/3}t^{1/6} + 103D^{1/2}(mt)^{1/6} + 7.45U_0^{1/2}(mt)^{1/2}\} \quad \ldots\ldots (1)$$

in which i_1 is the average limiting current in μA, n the number of electrons involved in the electrochemical reaction, C, the bulk concentration of electroactive species in mM, D its diffusion coefficient in cm²/sec, m the rate of flow of mercury in mg/sec and t the drop time in sec. In this equation the sum of the first and second terms in the brackets is less than 10% of the third term if U_0 is of the order of several cm/sec or greater. Thus if we neglect the first and second terms, equation (1) becomes

$$i_1 \simeq 1714n\,CD^{1/2}\,U_0^{1/2}\,(mt)^{1/2}. \quad \ldots\ldots\ldots\ldots (2)$$

This equation predicts that the limiting current involving maxima of the second kind is proportional to the concentration of the reducible substance and to the square root of the diffusion coefficient, and that it is independent of the mercury pressure. Experimentally all of these relations were found to be obeyed[1,2], but a direct comparison between observed and calculated limiting currents could not be made because the actual surface velocity U_0 is unknown.

Limiting currents in the presence of a surface-active substance

Maxima of the second kind can be eliminated by adding a suitable surface-active substance which is adsorbed on the mercury surface (*cf.* curve G in Fig. 2). The variation of the limiting current of thallium in 0.02M potassium nitrate at the RDME with varying concentration of gelatin is illustrated in Fig. 4. At a gelatin concentration of 0.008% the limiting current becomes constant. It is considered that at this and higher concentrations of gelatin its film is formed rapidly on the mercury surface, completely inhibiting the motion of the solution on the drop surface. Consequently, in the presence of sufficient gelatin the contribution of convection to the over-all rate of mass transfer is considered to be much smaller than in its absence. This results in a decrease of the limiting current upon the addition of gelatin, and it accounts for the facts that the limiting current varies only slightly with the potential of the mercury and is hardly affected by the ionic strength in the presence of the suppressor. The limiting anodic current at a rotated dropping thallium amalgam electrode was found to increase with the rate of rotation in the absence of gelatin but to remain unaffected by the speed of rotation in its presence[1]. The larger current at higher speeds of rotation in the absence of gelatin is considered to be caused by the fact that the tangential flow on the amalgam surface enhances a motion within the amalgam drop, whereas in the presence of gelatin this motion does not occur since there are no flow velocities on the amalgam surface.

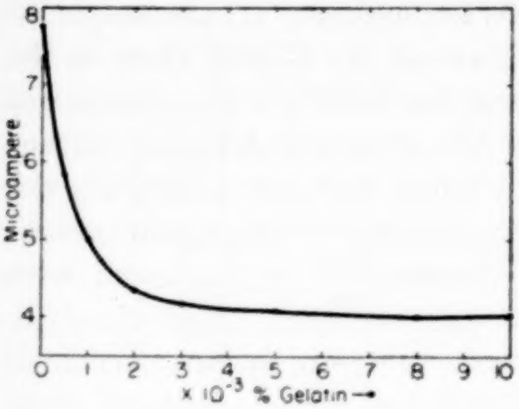

Fig. 4. Limiting current of thallium ($2.5 \cdot 10^{-5} M$ Tl_2SO_4, $0.02 M$ KNO_3, 300 r.p.m.) *vs.* gelatin concentration. Current measured at −0.7 V and corrected for residual.

As can be seen from the pronounced decrease of the limiting current in the range of even small concentrations of gelatin, the current involving the maxima is very sensitive to trace amounts of surface-active substances, which are usually present as impurity in a solution. Consequently, for most practical purposes it is imperative to suppress the maxima completely by adding a sufficient amount of a suitable surface active compound. When the maxima are thus eliminated, the limiting current-potential curve at the RDME resembles that at the DME. However, the quantitative dependence of the limiting current upon various factors such as m, t, or D is quite different at these two electrodes.

We derived the following equation at 25°C for the average limiting current which does not involve maxima[2]:

$$i_1 = 230nCD^{1/2}\{m^{2/3}t^{1/6} + 103D^{1/6}(mt)^{1/3} + 5.76D^{1/6}U^{1/2}\nu^{-1/6}(mt)^{1/2}\} \quad . \; . \; . \; . \quad (3)$$

in which U is the linear speed of rotation of the electrode in cm/sec and ν the kinematic viscosity of the solution in cm²/sec. The following assumptions were made in the derivation of this equation: (1) the mercury drop is an expanding perfect sphere, (2) there exists a laminar boundary layer around the mercury drop and (3) the tangential flow velocity outside the boundary layer is uniformly equal to the apparent speed of rotation of the electrode. An extensive test confirmed the validity of the above equation. Quantitative agreement within the experimental error between calculated and experimental data (*cf.* Table I) was found under the conditions that (1) the diameter of orifice is smaller than *ca.* 0.7 mm, (2) the distance between the orifice and center of rotation is smaller than *ca.* 8 mm, (3) the speed of rotation is 75 to 210 r.p.m. and (4) the kinematic viscosity is smaller than *ca.* 1.3 centistokes. The validity of the equation for the instantaneous limiting current

$$i_t = 230nCD^{1/2}\{(7/6)m^{2/3}t^{1/6} + (4/3)103D^{1/6}(mt)^{1/3} + (3/2)5.76U^{1/2}\nu^{-1/6}D^{1/6}(mt)^{1/2}\} \quad (4)$$

was also tested and a good agreement between observed and calculated curves was found except during the very early life of the drop.

In equation (3), the sum of the first and second terms in the brackets is about 15% or less of the third term when U is not too small. As a first approximation, therefore, we can write

$$i_1 \propto nCD^{2/3}U^{1/2}\nu^{-1/6}(mt)^{1/2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

If equation (3) or (5) is compared with the Ilkovic equation for the diffusion current at the DME

$$i_d = 607nCD^{1/2}m^{2/3}t^{1/6} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

the following differences between these two electrodes are evident: (1) the height of mercury has a much smaller effect on the limiting current at the RDME than on the diffusion current at the DME, (2) the limiting current at the RDME in the presence of a surface active substance is roughly proportional to $D^{2/3}$, while the diffusion current at the DME is closely proportional to $D^{1/2}$ and (3) the effect of the drop time on the limiting current at the RDME ($\sim t^{1/2}$) is much greater than that on the diffusion current at the DME ($t^{1/6}$). A value of the exponent of t of 0.56 instead of 0.50 was found with an electrode with the following characteristics: m = 7.79 mg/sec, t (open circuit in 0.1 M potassium chloride) = 4.54 sec, diameter of orifice = 0.5 mm, distance orifice to center of rotation = 5.16 mm, 210 r.p.m. We shall discuss further some of these factors which are of primary importance.

(a) *Effect of the drop time.* For practical analytical purposes it is unnecessary to use an electrode which obeys the theoretical equation described above. Actually electrodes with a larger orifice, which do not obey the equation, are more favorable for trace analyses because such electrodes are more sensitive than those with a small orifice, because at the former mercury drops with a larger surface are formed. Unfortunately at electrodes with such a large orifice the exponent of t tends to become even greater than 0.5, and may approach a value of one:

$$i_1 \cong kt^a \quad (a > 0.5) \qquad (7)$$

This increase of a with increasing orifice diameter can be attributed to a significant deformation from the spherical shape of the larger mercury drop. From the practical viewpoint the relationship between i_1 and t is important because of the variation of drop time with potential. Consequently, a limiting current at the RDME varies much more with potential than a diffusion current at the DME. As an example, the relative variation of the limiting current at two different electrodes of mercury(II) in 0.1 M nitric acid and that of thallium in 0.1 M potassium chloride in the presence of 0.01% polyacrylamide as a maximum suppressor (*vide infra*) with the potential is shown in Fig. 5. For comparison the relative change of the diffusion current with potential at the DME is also given. In conventional polarography with the DME the diffusion current may be assumed to be constant over the potential range from zero to —1.0 V *vs.* SCE, since the product $m^{2/3}t^{1/6}$ in the Ilkovic equation (6) is practically constant within this potential range[6] (see curve III in Fig. 5). The limiting current at the RDME can be assumed to be constant (±1%) only within the potential range from —0.3 to —0.8 V (see Fig. 5). The effect of drop time on the limiting current was less at electrode 1 than at electrode 2 (Fig. 5) since the a value [eqn. (7)] for the former was 0.56 and for the latter 0.84.

For a given electrode the exponent a can be determined empirically by measuring the limiting current over a wide range of potentials of a solution of a metal ion, *e.g.* mercuric chloride in potassium nitrate. The value of a is found as the slope of the plot of log i_1 *versus* log t. In a strict sense this plot should not give a straight line nor should the slope be the same for ions with different diffusion coefficients as is evident from equation (3). However, under experimental conditions, relation (7) holds so closely that the plot does yield a reasonably straight line whose slope is practically the same for various metal ions[5]. As was mentioned in a previous section, if this plot shows irregularities, the dimension and/or the preparation of the electrode are probably not correct.

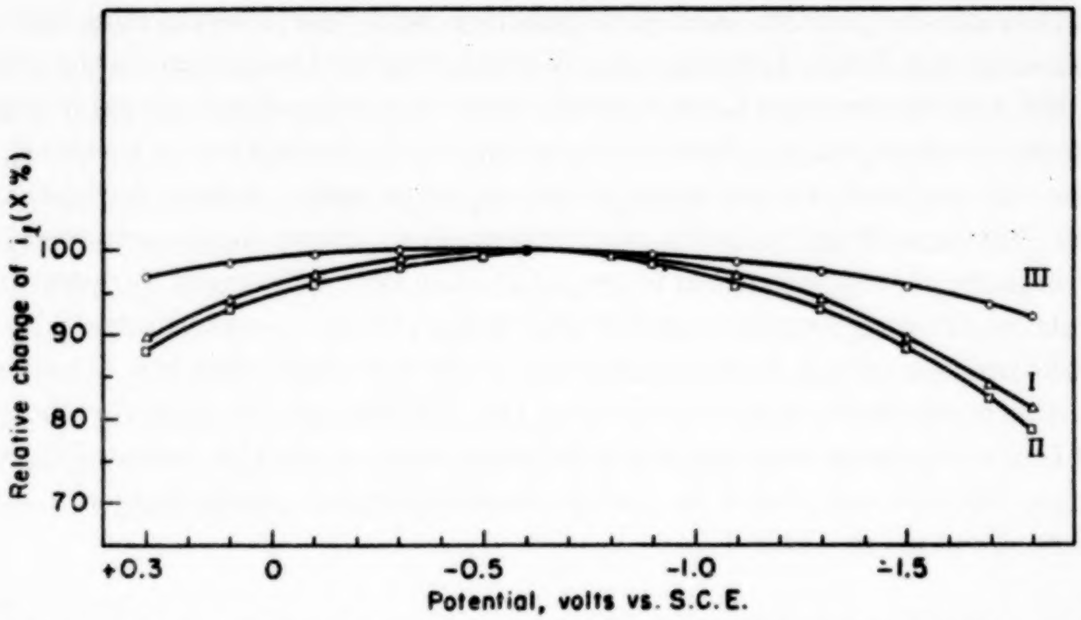

Fig. 5. Relative variation of limiting current with potential (determined with Hg(II) in 0.1 M HNO_3 and with Tl^+ in 0.1 M KCl both in the presence of 0.01% polyacrylamide). I, electrode 1; II, electrode 2; III, DME.

Once the value of a for a particular electrode is determined in this manner, the limiting current $(i_1)_2$ at a potential E_2 can be calculated from the limiting current $(i_1)_1$ at a more positive potential E_1 from the relation

$$(i_1)_2 = (i_1)_1 \, (t_2/t_1)^a \quad \ldots\ldots\ldots\ldots\ldots \quad (8)$$

in which t_1 and t_2 are the drop times at potentials E_1 and E_2, respectively.

(b) *Effect of the diffusion coefficient.* In the calculation of the limiting current with the aid of the theoretical equation (3) it is important to use D values which correspond to diffusion coefficients under the actual experimental conditions.

The D values at infinite dilution calculated from equivalent conductance data are often quite different from those under experimental conditions in polarography,

TABLE I

COMPARISON OF OBSERVED AND CALCULATED LIMITING CURRENTS

(Electrode: orifice diameter, 0.75 mm; *d*, 7.31 mm; 210 r.p.m.)

Ion	*Supporting electrolyte*	*$D \cdot 10^5$ cm²/sec*	*$\nu \cdot 10^2$ cm²/sec*	*C mM*	*m mg/sec*	*E volt*	*t sec*	*i_1(obs) µA*	*i_1(calc) µA*
Tl^+ [a]	0.005 M KCl	1.92	0.898	0.101	6.68	-0.9^c	5.45	5.59	5.71
Pb^{+2} [b]	1 M KCl	1.001	0.853	0.502	9.86	-0.7^d	3.99	39.0	39.4
	0.1 M KCl	0.970	0.892	0.507	12.19	-0.7^d	3.24	38.6	39.3
Zn^{+2} [b]	1 M KNO_3	0.73	0.825	0.400	9.83	-1.3^d	3.47	24.6	24.1
	0.05 M KNO_3	0.69	0.894	0.400	6.66	-1.5^c	5.43	22.7	23.4
	2 M KCl	0.940	0.825	0.400	9.86	-1.45^d	3.29	28.2	28.0
	1 M KCl	0.818	0.853	0.400	9.86	-1.35^d	3.40	25.4	25.6
	0.1 M KCl	0.729	0.892	0.400	12.19	-1.2^d	3.02	25.6	25.0
	0.01 M KCl	0.712	0.898	0.200	9.84	-1.3^c	3.72	11.8	12.1
Ni^{+2} [b]	0.1 M $NaClO_4$ + 0.001 M $HClO_4$	0.60	0.897	0.378	9.86	-1.3^d	3.52	20.3	19.9

[a] In the presence of 0.01% gelatin.
[b] In the presence of 0.01% starch.
[c] *Versus* mercury pool anode.
[d] *Versus* SCE.

although they are frequently used in connection with the Ilkovic equation and its modifications at the DME. Diffusion coefficients of various metal ions in the presence of excess indifferent electrolytes have recently been determined by several investigators using different techniques; *e.g.* the radiotracer method[7], the COTTRELL method[8], and the diaphragm cell method[9]. Unfortunately, the reported values differ considerably from each other. We tested[2] the validity of equation (3) by using these various values of D over a wide range of ionic strengths (0.005 to 2). The best agreement between observed and calculated limiting currents was found using the D values obtained by WANG[7] by the radiotracer method. It was concluded from this result that the D values determined by this method are reliable and that the RDME can be used for the determination of D of an electroactive species at different ionic strengths. Some of the values of the limiting current calculated by using tracer diffusion coefficients are compared with observed values in Table I.

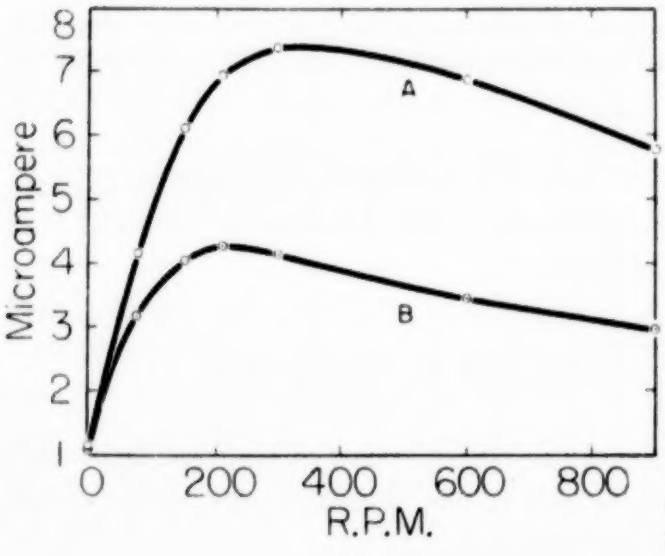

Fig. 6. Limiting current at RDME in $2.5 \cdot 10^{-5} M$ Tl_2SO_4, $0.02 M$ KCl *vs.* speed of rotation (r.p.m.): A, in absence; B, in presence of 0.01% gelatin. Current measured at −0.7 V and corrected for residual.

(c) ***Effect of rate of rotation.*** The variation of the limiting current of thallium in $0.02 M$ potassium chloride with the speed of rotation is illustrated in Fig. 6. Both in the presence and absence of gelatin the limiting current at a given potential attains a maximum value at a speed of 200 to 300 r.p.m., a further increase in speed resulting in a decrease of current. This decrease can be accounted for partly by the decrease of the drop time and hence of the surface area with increasing speed of rotation resulting from centrifugal force effects. Within the range from zero to about 300 r.p.m. this effect is overbalanced by the rapid increase of convective transfer, causing an over-all increase in average limiting current. In addition to the drop time effect, the swirling motion of the solution by the fast rotation of the electrode is probably responsible for the lower limiting current at higher speeds of rotation. It is evident that the electrode serves as an effective stirrer particularly at a high speed of rotation, giving rise to a swirling motion of the solution in the same direction as the rotation of the electrode. Thus the effective speed of the electrode *relative* to the solution will be much smaller than the apparent speed of rotation when the solution is vigorously stirred.

It has been mentioned already that the theoretical equation (3) holds only between 75 and 210 r.p.m. The discrepancy at higher speeds of rotation can be accounted for, at least partly, by the effect of the swirling.

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The sensitivity of the RDME in the presence of a surface-active substance at a suitable speed of rotation (200 to 300 r.p.m.) is of the order of ten times greater than that of the DME. The high limiting currents at the RDME are accounted for by both its larger surface area and by a higher rate of transport of electroactive species to the electrode. For example, the average area of a typical DME is of the order of 0.02 cm², while that of the RDME at 210 r.p.m. is about 0.05 cm². The "effective thickness of diffusion layer" ($\delta = nF\bar{A}DC/i_1$, where $\bar{A}$ is the average area of the mercury drop)[10] of the DME is of the order of 0.058 mm, while that of the RDME is 0.016 mm. Thus the average area of the mercury drop at the RDME is about three times as large as that at the DME, whereas the thickness of the diffusion layer is about 1/3.6 of that at the DME. These two factors give the RDME in the presence of a suppressor a sensitivity of the order of ten times as large as that of the DME.

Residual current

Residual currents at the RDME in general are a few times larger than those at the DME. The larger residual current at the RDME is attributed to both the larger faradaic component resulting from traces of reducible impurities in the solution and the larger condenser current component. The faradaic current component of the residual current at the RDME is of the order of ten times as great as that at the DME. The condenser current component should not be affected by the rotation, but the larger m value at the RDME causes a larger condenser current as is evident from the expression[11]

$$i_c = 0.0085\ km^{2/3}t^{-1/3}(E_{\max} - E) \quad \ldots\ldots\ldots\ldots \quad (9)$$

where i_c is the average condenser current in μA and k the capacity of the double layer at the mercury-solution interface in microfarads/cm². Assuming that the capacity in $0.1M$ potassium chloride is equal to 22 microfarads/cm² at the negative side of the isoelectric point[11], we calculate, as an example, the condenser current at one of our electrodes (m = 11.19 mg/sec, t = 4.14 sec at 210 r.p.m.) at —1.0 V *vs.* SCE to be 0.28 μA. The residual current actually observed in $0.1M$ potassium chloride was 0.48 μA, at —1.0 V. Accordingly the faradaic component becomes 0.20 μA. On the other hand, the condenser current at a DME (m = 2 mg/sec, t = 4.14 sec) is calculated to be 0.09 μA at the same potential. If we assume that the faradaic current at the DME is ten times smaller than that at the RDME, the total residual current at the DME is calculated to be 0.11 μA, as compared to 0.48 μA, the residual current found at the RDME. By further purification of the solvent and the supporting electrolyte, the faradaic part of the residual current at the RDME can be further reduced. For practical purposes this special purification is not necessary; we found that the residual current at the RDME could be measured with a precision of ± 0.02 μA.

The residual current-potential curve determined with $0.1M$ potassium chloride with the RDME was perfectly linear between —0.3 and —1.4 V and was parallel to the condenser current line calculated with the aid of equation (9), the slope being 0.60 μA/V[5].

Half-wave potential

A plot of $\log\{i/(i_1 - i)\}$ *vs.* potential for a thallium wave in the presence of gelatin at 300 r.p.m. at 25°C yielded[1] a straight line of slope 0.061, indicating that the thallium wave at the RDME analyzes in the same way as it does at the DME, and that the wave equation has a form similar to that derived for the DME.

$$E_{\mathrm{RDME}} = E_{1/2} - \frac{0.059}{n} \log \frac{i}{i_1 - i} \quad \ldots\ldots\ldots\ldots \quad (10)$$

where $E_{1/2}$ is given by

$$E_{1/2} = E_{\mathrm{a}}^{\circ} - (0.059/n)\log a_{\mathrm{Hg}} - (0.059/n)\log(f_{\mathrm{a}}/f_{\mathrm{s}}) - (0.059/n)\log\,(k_{\mathrm{s}}/k_{\mathrm{a}}) =$$
$$E' - (0.059/n)\log\,(k_{\mathrm{s}}/k_{\mathrm{a}}) \quad \ldots\ldots\ldots\ldots \quad (11)$$

where k_{s} and k_{a} are proportionality constants, relating current and concentration of ion in solution and metal in mercury, respectively.

When the RDME is not rotated it behaves essentially like a DME. For such an electrode the ratio $k_{\mathrm{s}}/k_{\mathrm{a}}$ is closely equal to $(D_{\mathrm{s}}/D_{\mathrm{a}})^{1/2}$, where D_{s} and D_{a} are the diffusion coefficients of the metal ion in the solution and the metal in mercury respectively. Thus from the experimental value of $E_{1/2}$ at the unrotated RDME and the values of D_{s} and D_{a}, E' in equation (11) can be calculated. The value of k_{a} at various speeds of rotation can then be evaluated by using experimental values of k_{s}, which are determined from the limiting current measurements, and those of $E_{1/2}$ from equation (11). Such values for thallium in 0.02*M* potassium nitrate in the presence of gelatin are listed in Table II.

It is seen from this table that the k_{a} values are practically constant and independent of stirring in the presence of a suppressor. This observation agrees with the experimental fact mentioned already that the limiting anodic current at a rotated dropping amalgam electrode is not affected by the rotation of the electrode. Table II also indicates that the $E_{1/2}$ values are practically independent of the speed of rotation between 75 and 900 r.p.m. The large difference in k_{s} value in equation (11) between the rotated and unrotated electrodes accounts for the shift of 30 mV of the half-wave potential of thallium caused by the rotation.

TABLE II

HALF-WAVE POTENTIALS AND PROPORTIONALITY CONSTANTS k_{s} AND k_{a} OF THALLIUM AT A RDME AT VARIOUS SPEEDS OF ROTATION

All solutions were $5 \cdot 10^{-5}$ *M* in Tl^+, 0.02*M* in KCl, and 0.01% in gelatin. k_{s} and k_{a} refer to m*M* solutions

r.p.m.	$E_{1/2}$, *V* *vs. SCE*	k_s	k_a
0	—0.452[a]	22.2	15.5
75	—0.484	63.0	12.7
150	—0.486	80.8	15.1
210	—0.485	85.6	16.6
300	—0.484	82.4	16.6
600	—0.482	69.5	15.1
900	—0.480	59.4	14.0

[a] $E_{1/2}$ at DME is —0.451 V in 0.02*M* KNO_3.

It is expected that the half-wave potential should not be affected by rotation when the oxidized and reduced forms in a reversible electrode reaction are both soluble in the aqueous phase. Thus, for instance, the half-wave potential of the anodic cysteine wave which corresponds to the dissolution of mercury to form mercurous cysteinate was found practically the same at both the RDME and the DME[1].

Solutions of cysteine in 0.05 M borax, pH 9.2, gave a half-wave potential of —0.510 V ± 3 mV at the RDME (300 r.p.m.) as compared to —0.520 V at the DME[1].

Selection of maximum suppressor

For general analytical purposes it is desirable to have available a maximum suppressor which remains adsorbed on the mercury surface between the dissolution potential of mercury and the decomposition potential of the supporting electrolyte. In addition, there must be no interfering chemical interaction between the capillary active substance and the species to be analyzed.

If the surface active substance is desorbed at a certain potential from the mercury surface, a desorption wave appears in the current - potential curve; the current begins to rise at a potential where the desorption starts and, upon its complete desorption, coincides with the current - potential curve obtained in the absence of surface-active compounds. An extensive investigation being performed in this laboratory with a large number of surface-active compounds revealed that the majority of these compounds exhibit desorption waves at potentials more positive than about —1.6 V *vs.* SCE. A few examples of desorption waves observed at the RDME are shown in Fig. 7.

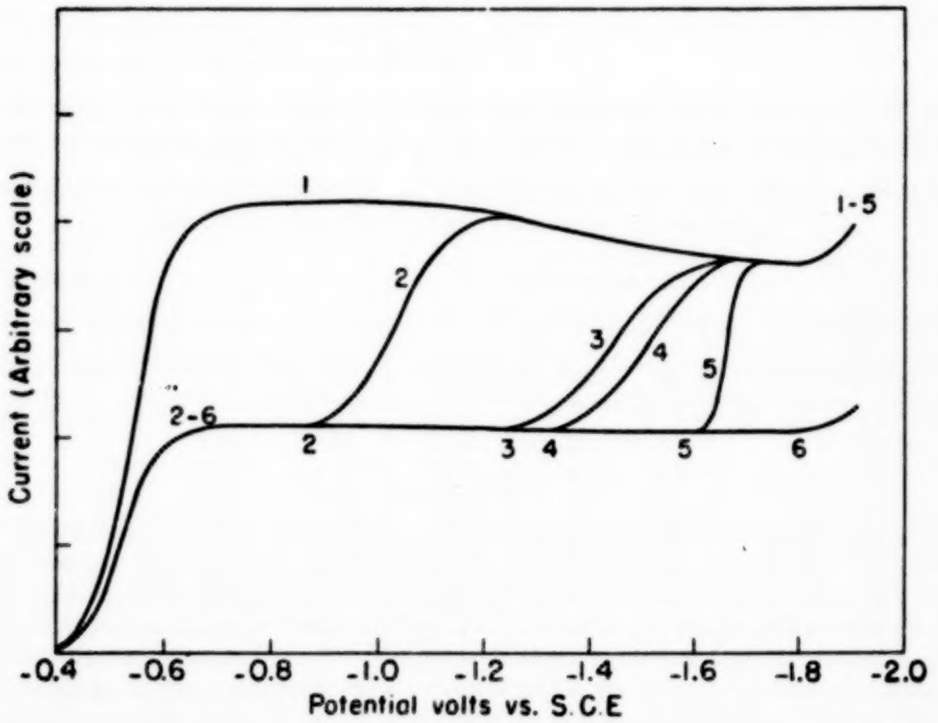

Fig. 7. Desorption waves of several surface active substances. (All curves were obtained with thallium in 1 M $NaClO_4$ at 150 r.p.m. at 25°C.) 1, No surface-active substance; 2, naphthalene (saturated, *ca.* 0.003%); 3, starch (0.005%); 4, agar (0.01%); 5, Triton X-100 (0.01%); 6, gelatin (0.01%), or polyacrylamide (0.01%).

The polarographic characteristics of surface-active substances and their desorption waves are being studied and further details will be described in a subsequent paper. Evidently surface active substances which give desorption waves are unsuitable for general use at the RDME.

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Gelatin does not exhibit a desorption wave and would seem to be ideally suitable as a maximum suppressor. However, under certain conditions, particularly at the negative side of its isoelectric point, gelatin tends to combine chemically with some metal ions and thus decreases the limiting current. This effect is rarely noticed at the DME because as a rule the ratio of concentrations of gelatin to metal ion is so small that the decrease of free metal ion concentration is negligible. At the RDME where concentrations of electroactive species can be some ten times smaller than at the DME, this effect can be pronounced. In a systematic study of many capillary-active substances, we found that polyacrylamide (PAM 75, American Cyanamid Co., New York) is an ideal maximum suppressor[5]. It remains adsorbed over the entire potential range which can be covered at the RDME and DME, and it does not combine with metal ions or other constituents tested so far. Maxima at the RDME are suppressed completely by 0.01% polyacrylamide. Its aqueous solution is perfectly clear and stable, and no excessive foaming takes place when nitrogen is passed through. This substance is recommended for polarographic work both at the DME and at the RDME. As an illustration of the adverse effect of gelatin, results obtained with copper in ammoniacal medium in the presence of this suppressor are compared with those in the presence of polyacrylamide in Table III. It is seen that with gelatin the i_1/C value increases markedly with copper concentration, while with polyacrylamide it is perfectly constant at various metal concentrations.

TABLE III

PROPORTIONALITY BETWEEN THE LIMITING CURRENT AND THE CONCENTRATION OF COPPER IN AMMONIACAL MEDIUM IN THE PRESENCE OF GELATIN AND POLYACRYLAMIDE

Potential, -0.7 V *vs.* SCE; supporting electrolyte, 0.1 M ammonia and 0.1 M ammonium nitrate; 210 r.p.m. currents corrected for the residual.

Concn. of copper mM	*Gelatin*						*Polyacrylamide*			
	0.01%		*0.02%*		*0.04%*		*0.01%*		*0.02%*	
	$i_1(\mu A)$	i_1/C	$i_1(\mu A)$	i_1/C	$i_1(\mu A)$	i_1/C	$i_1(\mu A)$	i_1/C	$i_1(\mu A)$	i_1/C
0.00400	0.26	65	0.22	55	0.18	45	0.34	85	0.33	84
0.00800	0.60	75	0.53	66	0.40	50	0.68	85	0.67	84
0.0160	1.20	75	1.08	68	0.91	56	1.36	85	1.34	84
0.0320	2.48	77.5	2.38	74.4	2.05	64.2	2.72	85.0	2.70	84.4
0.0640	5.22	81.5	4.92	76.9	4.44	69.3	5.34	83.5	5.36	83.8
0.0960	7.92	82.5	7.61	79.3	6.94	72.3	8.13	84.7	8.10	84.3
0.128	10.7	83.6	10.2	80.0	9.55	74.6	10.8	84.4	10.8	84.4

It is possible to estimate the number of moles of copper bound to a unit quantity of gelatin under our experimental conditions. A plot of i_1 against concentration of copper in the presence of 0.04% gelatin yields a curve at the lower copper concentrations, but it becomes reasonably straight above $2 \cdot 10^{-4} M$ copper. In the presence of polyacrylamide i_1/C remains constant, even at the smallest copper concentrations. From the difference between the i_1-C line in the presence of 0.04% gelatin and that in the presence of 0.01% polyacrylamide it was estimated that approximately $2 \cdot 10^{-5}$ mole of copper is bound per 1 g of gelatin.

Analytical applications

Table III also illustrates the lowest order of concentration of an electroactive species which can be determined satisfactorily at the RDME. When oxygen was completely removed by passage of oxygen-free nitrogen through a glass-fritted disk into the solution, the residual current could be measured with a reproducibility of $\pm 0.02\ \mu$A. Limiting currents of the order of $3\ \mu$A or greater have been measured with a precision of $\pm$ 1.5%. Concentrations of the order of $10^{-5}N$ ($i_1 - i_r$ of the order of $0.3\ \mu$A) have been measured with an accuracy and precision of the order of 4 to 5%, concentrations of the order of $10^{-4}N$ or greater with an accuracy and precision of 1 to 2%. A more exact treatment of accuracy and precision will be given in a subsequent paper[5]. When dealing with a mixture of electroactive constituents, the wave which appears at the most positive potential is measured with the above accuracy and precision. The accuracy becomes less for subsequent waves, as is also the case at the DME. As has been discussed in a previous section the correction to be applied for the variation in drop time in the calculation of the limiting current of the first wave at a more negative potential is considerably greater for the RDME than for the DME.

In the analysis of a mixture of two species, the limiting current of the substance which produces the second wave is equal to the total current (corrected for the residual current) at a potential in the limiting current plateau region of this substance minus the limiting current which the substance producing the first wave would have at this potential. The latter can be estimated with a probable error less than about $\pm$ 2%[5] by employing equation (8) or making use of Fig. 5. The same principle applies to a mixture of several reducible substances.

As an example of analysis under fairly extreme conditions we report the results obtained by Dr. T. FUJINAGA in this laboratory in a mixture (of unknown composition to him) which was $8.38 \cdot 10^{-5}M$ in thallium(I) and $4.08 \cdot 10^{-5}M$ in manganese. After proper consideration of the effect of drop time a composition of $(8.27 \pm 0.04) \cdot 10^{-5}M$ in thallium and $(4.03 \pm 0.03) \cdot 10^{-5}M$ in manganese was derived from three independent determinations of the current-potential curves. This good agreement illustrates the usefulness of the RDME for the analysis of mixtures containing traces of electroactive constituents. Details of Dr. FUJINAGA's work will be presented in a subsequent paper[5].

SUMMARY

The various factors which affect limiting currents at the rotated dropping mercury electrode (RDME) are reviewed. The current at the RDME in the absence of surface active substances involves maxima of the second kind, even under conditions where these maxima are not observed at the conventional dropping mercury electrode (DME). For most practical purposes, it is necessary to eliminate the maxima completely by adding a suitable surface active compound. The presence of 0.01% polyacrylamide is recommended as a maximum suppressor in all polarographic work. At a suitable speed of rotation (200 to 300 r.p.m.) the sensitivity of the RDME in the presence of a surface active substance is about ten times as great as that of the DME.

Equation (3), derived in a previous paper[4] accounts quantitatively for the relation between limiting current in the presence of a suitable maximum suppressor on the one hand and the concentration and diffusion coefficient of electroactive species, speed of rotation, kinematic viscosity and the characteristics of the electrode (m and t) on the other. The limiting current is practically independent of the pressure of mercury, but varies with t^a, where $a \geq 0.5$.

For reversible reactions half-wave potentials at the RDME are of the same order of magnitude as observed at the DME. The slight difference observed in the reduction of metal ions to metal amalgams is accounted for quantitatively by the larger rate of transport of electroactive species to the RDME.

The RDME is recommended for the analysis of solutions containing one or more electroactive species in concentration of less than about $10^{-4}N$. For markedly higher concentrations the DME is generally preferred.

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DISCUSSION

Prof. H. A. Laitinen (Urbana):

I would have expected that the value of m would be determined by the length and diameter of the constricted portion of the capillary, and that the drop time would be determined by the diameter of the orifice, because the diameter of the orifice should primarily determine the volume of the drop, while the constricted portion should determine the rate of flow.

Prof. I. M. Kolthoff:

Actually the value of m appears to be mainly determined by the diameter of the orifice, and t by the capillary.

Dr. H. Berg (Jena):

Die neue Elektrode umgeht Schwierigkeiten der Heyrovsky-Tropfelektrode: Verarmung und Abschirmung (keine Maxima 1. Art), hat dagegen andere besondere Probleme:

(a) Adsorbierbare Depolarisatoren dürften wegen der Beeinflussung der Stufenhöhe keine linearen Eichkurven ergeben.

(b) Die *i-t* Kurve des Einzeltropfens zeigt undefinierte Stromschwankungen, was auf spezielle Strömungen (Wirbel) am Tropfen hindeutet.

(c) Wegen (a) und (b) dürfte die theoretische Behandlung dieser Elektrode auf unüberwindliche Hindernisse stossen, welche noch nicht einmal für die normale Tropfelektrode völlig beseitigt sind. Wie äussern sich kinetischen Ströme allgemein an dieser Elektrode? Bestehen Beziehungen zur strömenden Elektroden?

Prof. I. M. Kolthoff:

(a) We recommend to add for all practical purposes a suitable maximum suppressor. Under this condition the electroactive substance may be capillary-active.

(b) Not in the presence of the suitable suppressor.

(c) The theoretical derivation has just been published in the *J. Am. Chem. Soc.* Kinetic currents at the RDME will be studied in the near future.

Prof. B. Breyer (Sydney):

(1) The elimination of the oxygen maximum at the rotating dropping mercury electrode could be due to the presence of silicone. Similar observations have been made by ourselves using ordinary dropping mercury electrodes which have been treated with silicone.

(2) Desorption potentials of surface active substances can be measured with great accuracy by the use of our tensammetric method.

(3) In the equation derived for the rotating electrode there appear the term $(mt)^{1/3}$ which implies that the current obtained should be independent of the height of the mercury reservoir. Has this been confirmed by experiment?

(4) Has Prof. Kolthoff also observed the fact that the presence of gelatine has no effect on the discharge of the Tl^+-ion?

Prof. I. M. Kolthoff:

(1) We plan to study the effect of silicone on maxima of the first kind at the conventional DME. It is also possible that there is little shielding around the drop at our RDME because of shape of the orifice.

(2) We do not claim that "desorption waves" take the place of other methods.

(3) Yes; if you use the approximate equation.

(4) Yes.

THE USE OF THE ROTATED DROPPING MERCURY ELECTRODE IN POLAROGRAPHIC ANALYSES AND AMPEROMETRIC TITRATIONS OF MICROMOLAR SOLUTION

by

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INTRODUCTION

Recently STRICKS AND KOLTHOFF[1] devised a new electrode in polarography, called rotated dropping mercury electrode (RDME), and reported an extensive fundamental work on the characteristics of the electrode and also on the polarography at the electrode. They state that the RDME combines the advantages of the conventional dropping mercury electrode (DME) with those of the rotated platinum electrode, the sensitivity of the RDME being made at least ten times greater than that of the DME.

In the present investigation, the characteristics of the RDME have been reinvestigated by means of a conventional direct current (D.C.) polarograph, a mechanical oscillograph, and a BREYER's alternating current (A.C.) polarograph[2]. The polarographic method with a D.C. polarograph has been applied to the determination of a minute quantity of lead contained in high-purity electrolytic zinc. Amperometric titrations have been carried out using the RDME as an indicator electrode, and an availability of the electrode in A.C. polarography has been examined. The results obtained are presented in this paper.

EXPERIMENTAL

Conventional current - voltage curves were recorded with a Yanagimoto Model PB-4 pen-recording polarograph. A polarograph synchronizer constructed by Yanagimoto Co. Ltd. was attached to the polarograph, when this was necessary. The recording of the current - time curve during the life of a mercury drop was made by means of a Yokokawa N-6 type mechanical oscillograph with a galvanometer period of 0.007 sec. For the measurement of BREYER's A.C. polarograms, a Yanagimoto Model GR-3 Galvarecorder with an automatically scanning potentiometer attached was used. A manual equipment[3] was set up for amperometric titrations.

The rotated dropping mercury electrodes used in this study were similar to those reported by STRICKS AND KOLTHOFF[1], which were driven by means of a syncronous motor (Type A, provided with gears for speeds of 100, 150, 200 and 300 r.p.m., constructed by Yanagimoto Co. Ltd.). They had the characteristics given in Table I, being measured, unless otherwise stated, in de-aerated 0.1 M potassium chloride solutions with open circuit.

In the measurement of D.C. polarograms and in amperometric titrations, the cell was connected with the saturated calomel electrode (S.C.E.) by a HUME AND HARRIS-type salt bridge[4]. When no contamination of chloride ions was desirable, the intermediate

TABLE I

CHARACTERISTICS OF THE ELECTRODES

Electrode	*Height of mercury head*	*m*	*t*		
			at 100 r.p.m.	at 150 r.p.m.	at 200 r.p.m.
A	40.0 ± 0.1 cm	4.96 mg/sec	7.22 sec	5.72 sec	3.54 sec
B	36.0 ± 0.1	10.82	3.47	—	—
C	42.0 ± 0.1	10.66	3.56	3.15	2.25
D*	35.5 ± 0.03	9.97	4.31	3.77	3.22

* Measured at potential of electrocapillary maximum.

agar plug, which was saturated with potassium chloride, was replaced by the one prepared with $1M$ potassium nitrate. In the measurement of A.C. polarograms, a mercury pool anode served as the reference electrode. Rates of change of applied potential were 3.33 mV/sec in the measurement of D.C. polarograms and 0.695 mV/sec in that of A.C. polarograms. Semi-microburets of 5-ml and 10-ml capacity were used for amperometric titrations. Purified nitrogen gas was passed through the solution to remove dissolved oxygen before the measurement, and over the surface of solution during the measurement. All polarographic measurements were carried out in a thermostat of 25° ± 0.1°C.

Standard solutions of copper, lead, cadmium and zinc were prepared from either metals or chemicals of analytical reagent grade. The concentration of the lead stock solution was determined gravimetrically. Dissodium ethylenediamine tetraacetate (EDTA) of analytical reagent grade (Wakō Pure Chemical Industries, Ltd.) was purified by recrystallization[5]. The stock solution of EDTA was $0.1M$ and this was standardized with the standard lead solution by amperometric titration, using the dropping mercury electrode as an indicator electrode[6]. Polyoxyethylene lauryl ether (LEO) with a mean mol. wt. of 862 was used for a maximum suppressor. The other chemicals used were all analytical reagent grade.

RESULTS

D.C. Polarography

Current – voltage curves of various concentrations of lead were obtained with Electrode A in de-aerated $0.1M$ and $1M$ KCl solutions containing $5 \cdot 10^{-6}M$ LEO. A proportionality between the concentration and the limiting current was obtained in the concentration range from $3 \cdot 10^{-4}M$ to $3 \cdot 10^{-7}M$ (Table II).

In order to apply this method to the determination of a minute quantity of lead contained in high-purity electrolytic zinc, a constancy of the i_1/c value was investigated in de-aerated $1M$ zinc chloride solutions in the presence of $5 \cdot 10^{-6}M$ LEO. A proportionality was found between the concentration and the limiting current, although the i_1/c values were somewhat smaller in this medium than those in $0.1M$ and $1M$ potassium chloride solutions.

High-purity electrolytic zinc was dissolved in concentrated hydrochloric acid in the presence of a trace of cobaltous chloride, and an excess of the acid was removed by

TABLE II

LIMITING CURRENT OF LEAD*

Conc. of lead	*at 100 r.p.m.*		*at 150 r.p.m.*		*at 200 r.p.m.*	
	i_1	i_1/c**	i_1	i_1/c**	i_1	i_1/c**
$2.94 \cdot 10^{-4} M$	17.03 μA	5.80	18.75 μA	6.38	17.91 μA	6.10
$2.94 \cdot 10^{-5}$	1.70_4	5.80	1.83_5	6.25	1.76	6.00
$2.94 \cdot 10^{-6}$	0.17_2	5.8_3	0.18_2	6.1_7	0.17_7	6.0_3
$2.94 \cdot 10^{-7}$	0.017_2	5.8_2	0.018_0	6.1	0.017_5	6.0

* Measured in $0.1 M$ KCl solutions containing $5 \cdot 10^{-6} M$ LEO with Electrode A.

** i_1/c is the limiting current in μA of $10^{-4} M$ solutions.

evaporation. The residue was dissolved into distilled water containing $5 \cdot 10^{-6} M$ LEO to make $1 M$ in concentration in regard to zinc chloride. The concentration of lead was determined directly from the i_1/c value, which was preliminarily obtained for lead in $1 M$ zinc chloride, and also by the standard addition method. Some of the results obtained are given in Table III.

TABLE III

LEAD CONTENT IN HIGH-PURITY ELECTROLYTIC ZINC

Samples	*Content of lead found*	
	from the i_1/c value	by standard addition method
No. 1	0.0007_1 %	0.0007_1 %
No. 4	0.0015_8	0.0015_4
No. 8	0.0013_7	0.0013_6
No. 10	0.0001_3	0.0001_3

It was already reported by STRICKS AND KOLTHOFF[1] that the limiting current at the RDME is markedly decreased by the addition of small amounts of gelatin. The same effect and tendency were observed with LEO. In the absence of surface active substance $0.979 \cdot 10^{-4} M$ of lead gave the limiting current of 13.53 μA in $0.1 M$ KCl solution at Electrode B at 100 r.p.m. Upon the addition of LEO, the limiting current decreased to 10.22 μA at $1 \cdot 10^{-6} M$ in concentration of LEO, to 6.80 μA at $5 \cdot 10^{-6} M$ and to 6.50 μA at $1 \cdot 10^{-5} M$. No further decrease of the limiting current was observed at concentrations of LEO greater than $1 \cdot 10^{-5} M$.

The half-wave potentials of the lead wave, on the other hand, remained constant unless the concentration of LEO exceeded $1 \cdot 10^{-5} M$.

Current - voltage curves of other metal ions were also measured in the supporting electrolyte with and without complex-forming anions. Proportionalities between the concentration and the limiting current were obtained in the range of concentration investigated.

Amperometric titrations

Amperometric titrations of copper, lead and cadmium were carried out with the EDTA solutions, using the RDME (Electrode C) as an indicator electrode. Acetate buffers of pH 4.75, ionic strength 0.1, containing $5 \cdot 10^{-6} M$ LEO (for lead and cadmium) or $2\cdot10^{-5}M$ LEO (for copper), served as supporting electrolytes. The EDTA stock solution was diluted with distilled water to adjust the concentration approximately ten times as great as those of the titrated ions.

In titrations, the current was measured at —0.15 V *vs.* S.C.E. for copper, at —0.60 V *vs.* S.C.E. for lead and at —0.75 V *vs.* S.C.E. for cadmium. The titration curves obtained were similar to those obtained with the DME[6,7]. Some of the results obtained with copper, lead and cadmium in the concentration range of $5\cdot10^{-4}M$ to $5\cdot10^{-6}M$ are given in Table IV.

TABLE IV

AMPEROMETRIC TITRATIONS OF COPPER, LEAD AND CADMIUM WITH ETHYLENEDIAMINETETRAACETATE

*Conc. of ions present**	*Conc. of EDTA solution*	*Vol. of EDTA sol. required*	*Conc. of ions found*	*Error*
$4.88\cdot10^{-4}M$ Cu	$4.94\cdot10^{-3}M$	5.94 ml	$4.89\cdot10^{-4}M$	+0.2 %
$4.88\cdot10^{-5}$	$4.94\cdot10^{-4}$	5.98	$4.92\cdot10^{-5}$	+0.6
$4.88\cdot10^{-6}$	$4.94\cdot10^{-5}$	6.00	$4.94\cdot10^{-6}$	+1.3
$4.90\cdot10^{-4}M$ Pb	$4.94\cdot10^{-3}$	6.00	$4.94\cdot10^{-4}$	+0.8
$4.90\cdot10^{-5}$	$4.94\cdot10^{-4}$	5.92	$4.89\cdot10^{-5}$	—0.2
$4.90\cdot10^{-6}$	$4.94\cdot10^{-5}$	5.76	$4.75\cdot10^{-6}$	—3.1
$5.00\cdot10^{-4}M$ Cd	$4.94\cdot10^{-3}$	6.07	$5.00\cdot10^{-4}$	0
$5.00\cdot10^{-5}$	$4.94\cdot10^{-4}$	6.08	$5.01\cdot10^{-5}$	+0.2
$5.00\cdot10^{-6}$	$4.94\cdot10^{-5}$	6.16	$5.07\cdot10^{-6}$	+1.4

* Initial volume is 60 ml.

A.C. Polarography

Breyer's A.C. polarograms were recorded with various concentrations of cadmium in de-aerated $1M$ potassium chloride solutions in the absence and presence of LEO at Electrode D rotated and unrotated. A typical example is given in Fig. 1, which was obtained with $2\cdot10^{-5}M$ cadmium in the presence of $8\cdot10^{-6}M$ LEO at rotation of 100 r.p.m.

The maximal currents given in Table V were measured in the presence of $8\cdot10^{-6}M$ LEO at 100 r.p.m. which indicate a proportionality existing between the concentration of cadmium and the maximal current in the range of concentration investigated.

TABLE V

MAXIMAL CURRENT OF CADMIUM*

Conc. of Cd	*Max. current*	i_{max}/c**
$1.0\cdot10^{-4}M$	17.90 μA	17.9
$5.0\cdot10^{-5}$	9.32	18.6
$2.0\cdot10^{-5}$	3.75	18.8
$1.0\cdot10^{-5}$	1.83	18.3
$5.0\cdot10^{-6}$	0.94_5	$18._9$
$2.0\cdot10^{-6}$	0.37_5	$18._8$
$1.0\cdot10^{-6}$	0.18_8	$18._8$

* Measured in $1M$ KCl solutions containing $8\cdot10^{-6}M$ LEO with Electrode D at 100 r.p.m.
** i_{max}/c is the maximal current of $10^{-4}M$ solutions.

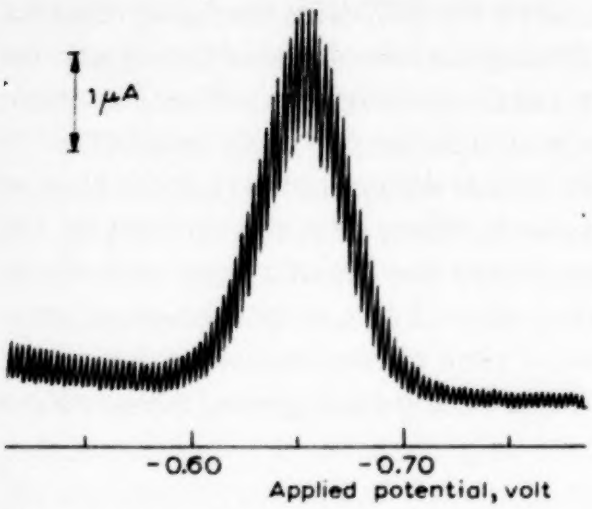

Fig. 1. A.C. polarogram of cadmium ($2 \cdot 10^{-5} M$) obtained at the RDME (Electrode D, 100 r.p.m.) in $1 M$ KCl solution containing $8 \cdot 10^{-6} M$ LEO.

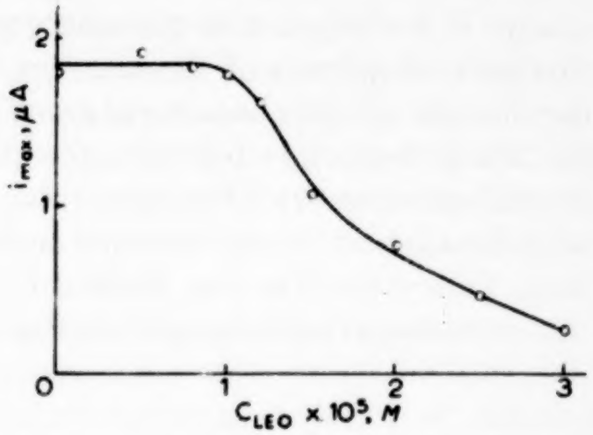

Fig. 2. Maximal current of cadmium ($1 \cdot 10^{-5} M$ Cd(II), $1 M$ KCl, 100 r.p.m.) *vs.* concentration of LEO.

The effect of LEO on the A.C. polarogram was, as was expected, entirely different from that on the D.C. polarogram. The wave heights of $1 \cdot 10^{-5} M$ cadmium, measured in the absence and with various concentrations of LEO, are plotted in Fig. 2. The wave heights remained nearly constant at concentrations of LEO up to $1 \cdot 10^{-5} M$, while, at concentrations over $1 \cdot 10^{-5} M$, they decreased with increase in concentration.

The A.C. polarograms obtained at various speeds of rotation indicated that the maximal current per unit mean surface area is independent of the speed of rotation unless the number of rotations exceeds 200 r.p.m. (Table VI). A somewhat smaller value obtained at the electrode unrotated may be attributed to a smaller mean surface area of the mercury drop.

TABLE VI

EFFECT OF SPEED OF ROTATION ON A.C. POLAROGRAMS

Speed of rotation	*Drop time*	*Mean surface area of mercury drop (A)*	*Maximal current* (i_{max})*	i_{max}/A
0 r.p.m.	5.32 sec	0.071 cm²	1.69 μA	23.7 μA/cm²
100	4.31	0.063	1.83	29.0
150	3.77	0.058	1.65	28.6
200	3.22	0.052	1.42	27.5

* Measured with $1.0 \cdot 10^{-5} M$ Cd in $1 M$ KCl solutions containing $8 \cdot 10^{-6} M$ LEO.

DISCUSSION

The usefulness of the RDME in polarographic analyses of minute quantities of electroactive species in solutions was already reported by STRICKS AND KOLTHOFF[1]. The present study has confirmed their statement by reinvestigating the characteristics of the electrode and by applying the electrode to the polarographic analysis of a minute quantity of lead contained in high-purity electrolytic zinc.

The availability of the RDME in amperometric titrations of micromolar solutions, which was also predicted by STRICKS AND KOLTHOFF[1], has been justified by the authors by applying the electrode as an indicator electrode to amperometric titrations of copper, lead and cadmium with disodium ethylenediamine tetraacetate solutions.

One of the disadvantages of the RDME is that, when the RDME is used, the recorder oscillates over a comparatively large amplitude during the life of each drop. A greater change in surface area of the mercury drop may partly contribute to this. However, this great amplitude of the recorder oscillations seems to be primarily attributed to the current – time characteristics of the RDME, which differs entirely from that of the DME. It is expected from the theoretical consideration that the current at the RDME increases with the square root of the time during the life of a drop and, therefore, the current – time curve for an individual drop should be a second-order of parabola. This prediction was verified by the current – time curves measured by means of a mechanical oscillograph. In Fig. 3 plots of log *i* *vs.* log *t* are given, whose slopes are approximately 0.5. A slight deviation from 0.5 may be explained by the fact that the actual RDME does not strictly satisfy the conditions that are assumed in the theoretical consideration.

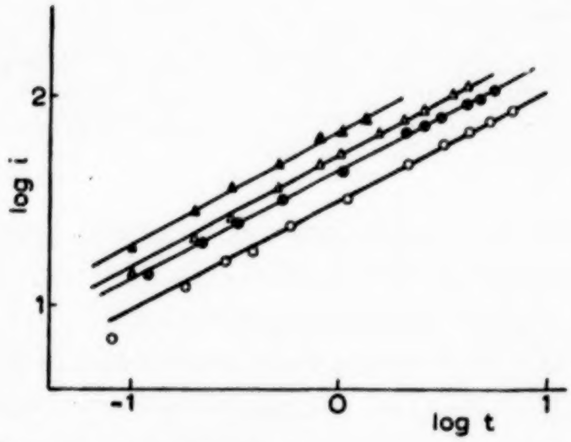

Fig. 3. Relation of log *i* *vs.* log *t* during the life of a mercury drop of the RDME: o, at 100 r.p.m.; ●, at 150 r.p.m.; △, 200 r.p.m.; ▲, at 300 r.p.m.

An increase in damping of the recorder was required to eliminate the large amplitude of recorder oscillations. However, this was not desirable from the standpoint of obtaining undeformed polarograms. Recently, YASUMORI* devised a new instrument, called polarograph synchronizer, with which the recorder oscillations can be eliminated without any distortion of polarograms, and he applied the instrument successfully to the measurement with the DME. The application of this device to the measurement with the RDME was undertaken by the present authors. The amplitude of recorder oscillations became much smaller, but the limiting current plateau was not so smooth as that obtained with the DME. This was considered due to the characteristics of the RDME. An abrupt increase in current, which occurs just before the mercury drop detaches from the capillary, and the existence of a threshold period at which the current remains constant at very low value, were observed on the current – time curves recorded by an oscillograph. The threshold period ranged from one-tenth to three-tenth second and was rather irregular depending on individual drops. These facts may be responsible for the irregularities which appeared on the current-voltage curves obtained with the polarograph synchronizer.

An equal increase in sensitivity for the oxygen wave might be another disadvantage of the RDME. Complete removal of dissolved oxygen was more difficult with the

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* Presented at the 10th Ann. Meeting of the Chemical Society of Japan, April, 1957.

RDME than with the DME. In this study, nitrogen gas was passed over the surface of solution during the measurement, but the concentration of oxygen in the solution more or less fluctuated as the rate of the flow of nitrogen gas changed.

In Breyer's A.C. polarography, oxygen yields such a small wave in acid and neutral solutions that the complete removal of oxygen is not necessary as far as the solution is buffered. The results in the present investigation agreed with this expectation. The analysis of metal ions whose concentrations were between $10^{-6}M$ to $10^{-5}M$ was attained more easily by the A.C. polarographic method than by the D.C. polarographic method.

It should be mentioned that the RDME is less advantagous when applied in A.C. polarography. It is interesting to study the experimental results, which indicate that the maximal currents of A.C. polarograms obtained with varied speeds of rotation are proportional to the mean surface area of the mercury drop (see Table VI). In other words, as has been predicted by theoretical treatment[8], the effect of rotation, *i.e.* the effect of convection, gives no increase in current. The relation between the concentration of LEO and the maximal current also certifies the fact that the maximal current of A.C. polarograms is not favorably affected by the convection (See Fig. 2). The rotation of the electrode has no advantage in A.C. polarography.

SUMMARY

The applicability of the rotated dropping mercury electrode in conventional direct current polarography, alternate current polarography, and amperometric titrations, has been investigated. The direct current polarographic method was applied to the determination of minute quantities of lead contained in high-purity electrolytic zinc, the lowest content of lead determined being 0.0001 %. It was confirmed that the rotation of the electrode has no advantage in alternating current polarography. Some characteristics of the electrode, revealed by the measurement of current-time curves, are also presented and discussed.

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DISCUSSION

DR. H. N. WILSON (Billingham):

What was the chemical constitution of the maximum suppressor LEO?

Prof. N. TANAKA:

Polyoxyethylene lauryl ether.

DR. T. FUJINAGA (Kyoto):

According to our experimental results on surface active substances at the Univ. of Minnesota, most of the detergents including LEO is desorbed below —1.8 V *vs.* S.C.E.

APPLICATION DE LA GOUTTE PENDANTE DE MERCURE À LA DÉTERMINATION DE MINIMES QUANTITÉS DE DIFFÉRENTS IONS

Communiqué préliminaire

par

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Les principes de la méthode polarographique de J. HEYROVSKÝ sont bien connus: le polarographe enregistre les courants de diffusion $i_d = f(E)$. On obtient des polarogrammes — sur des électrodes de mercure, dont l'une — le plus souvent la cathode — est une électrode à gouttes. Il existe une fonction linéaire entre le courant de diffusion et la concentration du dépolarisateur $i_d = k \cdot c$ calculée par ILKOVIČ.

Si les concentrations des substances analysées ne sont pas trop petites, la sensibilité du galvanomètre employé n'est pas grande, alors le courant de charge du condensateur, qui est celui de la goutte de mercure, qui se forme, s'amplifie et tombe périodiquement et d'une façon continue — n'est pas grand en comparaison avec le courant de réduction d'un dépolarisateur. La détermination des substances aux concentrations de l'ordre de 10^{-3} moles/l ne présente pas de difficultés.

Au cas où la concentration de la substance déterminée est beaucoup plus petite, il est nécessaire d'employer les grandes sensibilités du galvanomètre.

Le courant de charge d'une électrode à gouttes dépasse en ce cas, même considérablement, le courant de dépolarisation de la substance analysée. Ici surgissent les difficultés de la mesure de l'intensité du courant de dépolarisation, („onde") qui détermine la quantité de la substance dissoute. ILKOVIČ ET SEMERANO ont inventé un arrangement simple, qui permet de compenser le courant de charge (de capacité); mais même avec tout cela la méthode polarographique permet de déterminer la concentration d'un dépolarisateur jusqu'aux concentrations de l'ordre de 10^{-6} moles/l.

HEYROVSKÝ ET FOREJT ont inventé, il y a plus de 15 ans, la méthode oscillopolarographique. Cette méthode se distingue de la méthode polarographique — où les électrodes sont polarisées par le courant continu — par la polarisation avec un courant continu auquel est superposé un courant alternatif sinusoidal (50 c/s). Au lieu d'un galvanomètre on peut suivre le mécanisme d'électrolyse en utilisant un oscillographe cathodique. De cette façon les résultats d'analyse sont obtenus instantanément.

Cette méthode, très ingénieuse en principe ne put pas atteindre la sensibilité et la précision des résultats obtenus par la méthode polarographique. La méthode oscillopolarographique permet d'estimer les concentrations jusqu'à 10^{-4} moles/l. Elle surpasse la méthode polarographique, quant à la possibilité de distinguer des substances organiques ressemblantes en mélange, par exemple les isomères du nitrophénol, où les ions de Cd^{+2} et In^{+3} dans une solution, qui se dépolarisent sous influence d'un courant continu aux mêmes potentiels de demi-onde, $E_{1/2}$.

Bibliographie p. 111

Il faut mentionner ici une très intéressante méthode publiée par **Barker et Jenkins**[1], qui ont inventé le „square wave polarograph". C'est un polarographe très compliqué et très coûteux et même pas accessible jusqu'à ces derniers temps. Dans cet arrangement au courant continu est superposé un courant rectangulaire. J'évite les détails, mais il faut mentionner, que les auteurs ont réussi à estimer de très petites quantités d'ions, de l'ordre de 10^{-7} moles/l.

Pendant les études faites avec un arrangement oscillopolarographique, en utilisant une électrode avec une période très prolongée de dégouttement, nous avons constaté, que certaines réactions d'électrolyse donnent différentes images sur l'écran d'un oscilloscope, quand le temps de la formation d'une goutte est assez long.

Ceci nous a conduit à la nécessité de construire une électrode à gouttes, où une goutte pourrait pendre pendant un temps pratiquement infiniment long, même si cette goutte est polarisée par un courant alternatif. Cela nous a réussi, en couvrant le tube capillaire avec une couche très mince d'un vernis siliconique.

Les résultats préliminaires ont été publiés il y a quelques mois[2].

Il est connu, que les images oscillopolarographiques permettent de distinguer immédiatement les réactions réversibles et irréversibles d'après la position des entailles: symétriques ou non sur des courbes $\frac{\mathrm{d}V}{\mathrm{d}t} = \mathrm{f}\,(V)$.

L'étude du mécanisme des différents processus sur une goutte pendante en appliquant la méthode oscillopolarographique (par exemple d'oxydation des amalgames etc.) et surtout l'idée d'améliorer la sensibilité d'estimation analytique de cette méthode nous a conduit à la méthode d'agglomération antérieure par l'électrolyse des ions étudies sur la goutte. Cette idée était déjà mentionnée dans le travail de **Barker et Jenkins**[1]. On peut observer ces derniers temps différentes tentatives pour utiliser de pareilles méthodes avec le but de séparer les ions ou augmenter la sensibilité de la détection de différents ions, formant un amalgame[3-5]. Notre méthode pouvait être très bien réalisée à l'aide de notre goutte pendante.

Les résultats obtenus par cette voie, peuvent être divisés en deux parties:

(1) Obtenus avec un arrangement oscillopolarographique.

(2) Obtenus avec un dispositif où on enregistre le courant d'oxydation d'un amalgame formé.

PARTIE EXPÉRIMENTALE

Le dispositif

L'ensemble d'un dispositif oscillopolarographique qui permet la réalisation du premier problème est bien connu. Pour réaliser le second on peut utiliser un polarographe, qui permet d'enregistrer les polarogrammes non seulement en avant, mais aussi en arrière: par exemple LP55. L'électrode à goutte pendante et le vase sont simplement construits (Fig. 1).

Ce dispositif permet non seulement d'obtenir une goutte d'une grandeur variable, mais aussi d'une façon très simple permet de reproduire des gouttes de même grandeur, en pressant à l'aide d'une vis la quantité nécessaire de mercure. Les gouttes pendantes employées dans ce travail avaient un diamètre de 0.64 et 0.80 mm. Le poids correspondant des gouttes étant 1.9 et 3.8 mg et la surface 1.3 et 2.0 mm^2. L'application de la petite goutte donne de meilleurs résultats. La solution analysée se trouve dans un vase d'un volume de 3 à 15 ml avec un mélangeur magnétique permettant de régler la fréquence de rotation. Il est préférable que la température reste constante. Il est absolument nécessaire d'éloigner l'air dissous dans la solution pour éviter la réduction d'oxygène et la formation d'hydroxydes[6].

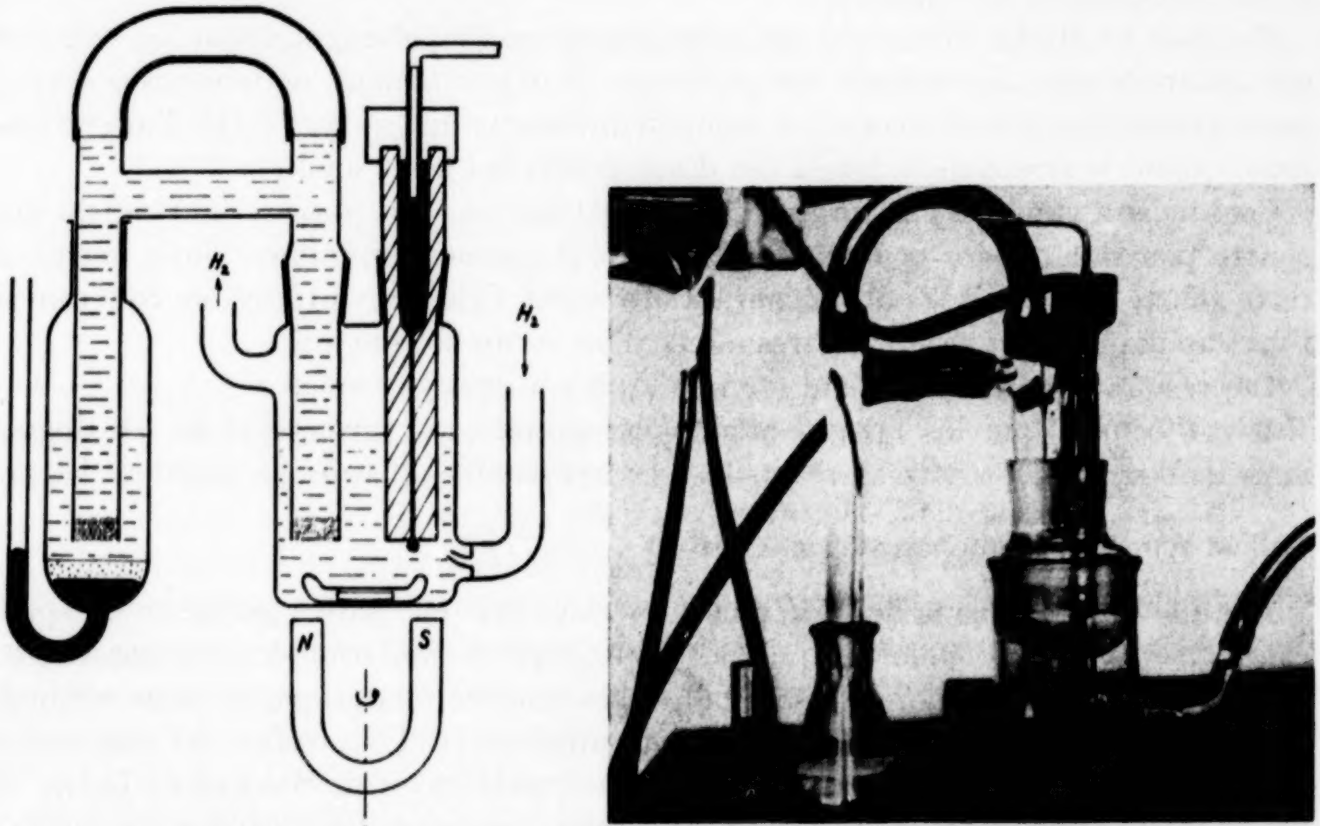

Fig. 1a et b. Schéma et la photographie du dispositif, avec électrode à goutte pendante et électrode au calomel.

Lingane a démontré[7] que le temps nécessaire pour déposer une certaine fraction des ions d'une solution (à l'aide du courant continu) dépend du coefficient de diffusion des ions D, qu'il est proportionnel au volume de la solution (inversement proportionnel à la concentration), inversement proportionnel à la surface d'électrode, dépend de l'intensité de l'agitation et est indépendant de la concentration initiale.

Il est évident, que l'agitation intense de la solution et une grande surface de l'électrode sont des conditions de la déposition rapide des ions sur la cathode.

La reproductibilité des résultats dépend de la possibilité d'obtenir des gouttes pendantes identiques.

Réactifs

La préparation de réactifs suffisamment purs pour nos buts était extrêmement difficile. Seulement l'électrolyse prolongée des solutions de base à l'aide d'un potentiostat sur des électrodes de mercure pouvait les purifier suffisamment.

Ces conditions étant prises en considération, voici les résultats obtenus.

Les expériences

La première série d'expériences obtenue avec un arrangement oscillopolarographique, les ions étant déposés préalablement par un courant continu, donne les résultats suivants.

On peut distinguer ici deux cas:

Le premier. Les ions sont déposés réversiblement et forment un amalgame. Si la concentration des ions est petite on n'observe pas d'entailles. Après une électrolyse prolongée avec le courant continu, la concentration de l'amalgame diminue très rapidement après la connection des électrodes avec la source du courant alternatif. Les entailles disparaissent complètement pendant des secondes. Dans ce cas on peut tirer des conclusions seulement en employant un écran fluorescent avec un temps très prolongé de fluorescence pour pouvoir mesurer une entaille maximum. Cette méthode est simple et augmente considérablement la sensibilité de détection.

Le second. Les ions sont déposés, donnant des entailles sur des courbes $\frac{dV}{dt} = f(V)$. Un exemple subtilement étudié par nous concerne les ions lithium en présence des ions aluminium. Les entailles résultent d'un processus dont le mécanisme n'est pas encore bien clair. En ce cas les entailles se distinguent par une persistance très grande et elles *grandissent* avec le temps de polarisation d'une goutte. Ceci permet de mesurer les entailles exactement après un temps approprié. On peut utiliser ce phénomène pour déterminer les ions aluminium et lithium.

La détermination de l'aluminium d'une concentration d'environ 10^{-4} mole/l en solution aqueuse $4M$ de LiCl est déjà possible, mais dans ces conditions l'apparition des entailles dépend:

(a) du temps du mélange des solutions (après une heure les entailles ne paraissent plus) et

(b) du temps de polarisation (les autres entailles aux potentiels plus positifs paraissent) (Fig. 2).

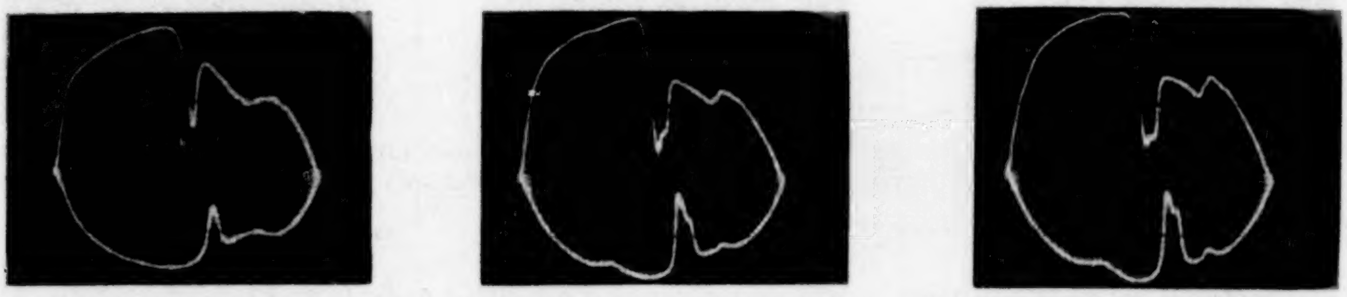

Fig. 2. Entailles obtenues dans une solution d'ions aluminium $10^{-4}M$ en solution de LiCl $4M$: (a) après 0 sec, (b) après 45 sec, (c) après 120 sec (à gauche -2.0 V; à droite 0 V).

La reproductibilité des entailles n'est pas bonne si la concentration d'aluminium est plus petite que 10^{-3} mole/l. Par exemple, en présence d'une solution d'aluminium $2 \cdot 10^{-4}M$, au cours de temps se forment même quatre entailles (Fig. 3).

Si la concentration de l'aluminium devient plus grande, par exemple $6 \cdot 10^{-4}$ mole/l, les images ressemblent à la Fig. 2.

Les oscillo-polarogrammes deviennent plus simples quand la concentration de l'alu-

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minium est plus grande. Dans ce cas il y a seulement une entaille, grandissante avec le temps d'électrolyse. La position de cette entaille change, si on change le potentiel limitant appliqué.

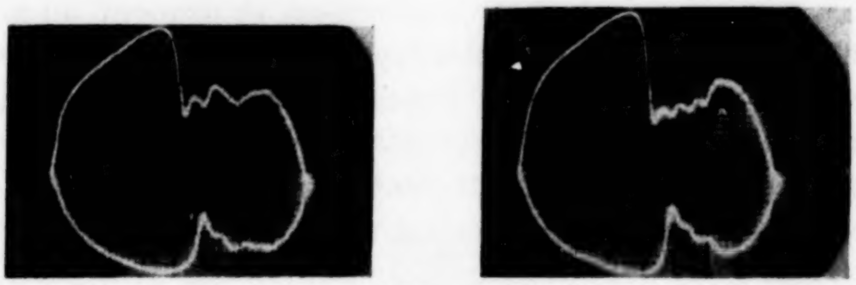

Fig. 3. Entailles obtenues dans une solution d'ions aluminium $2 \cdot 10^{-4}M$ en LiCl $4M$; (a) après 60 sec, (b) après 120 sec.

Quand la concentration des ions Al^{+3} est à peu près $10^{-2}M$, les entailles paraissent lentement, parce que la grande quantité des ions aluminium ne permet pas à la cathode d'atteindre immédiatement le potentiel de —2.0 V, nécessaire pour obtenir des entailles.

Dans des solutions des ions aluminium encore plus concentrées, à cause de cela, les entailles ne se forment plus. Ceci permet d'estimer la présence et la concentration d'aluminium dans la solution analysée.

On peut se servir du même phénomène pour *la détermination du lithium*. La réaction est spécifique et la détection d'ions lithium, même en concentration $10^{-5}M$, est possible. Les entailles se forment en présence des ions de Na^{+}, Ca^{+2}, Ba^{+2}, Cl^{-}, Br^{-}, NO_3^{-}, SO_4^{-2}, ClO_4^{-}. La meilleure composition de la solution est: KCl $1.25M$ en présence de la concentration $1 \div 2 \cdot 10^{-3}M$ des ions aluminium. On peut estimer la concentration des ions lithium d'après le temps d'apparition des entailles et leur grandeur (Fig. 4).

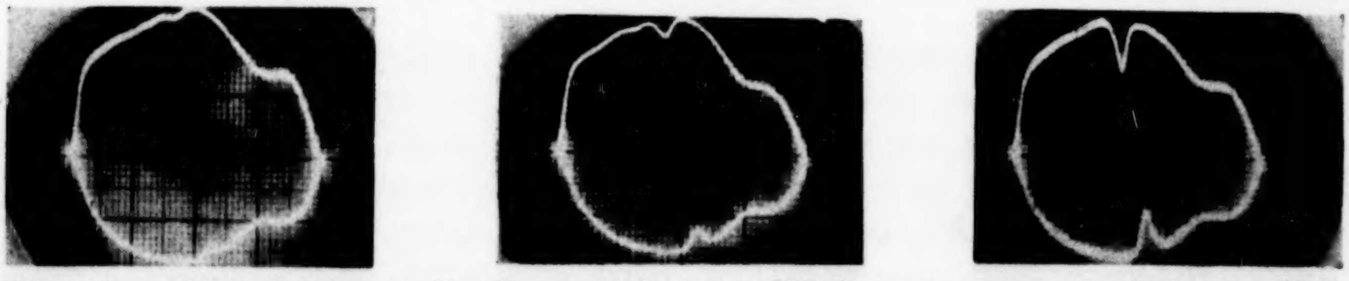

Fig. 4. Agrandissement des entailles dans une solution $10^{-3}M$ d'ions aluminium en solution $1.25M$ de KCl: (a) solution d'ions lithium $10^{-5}\ M$ après 5 min, (b) $2 \cdot 10^{-5}M$ après 3 min et (c) $5 \cdot 10^{-5}M$ après 2 min.

Quelques ml de la solution, même en présence d'air suffit pour faire une estimation. Il est évident sur ces résultats, que la fraction d'un microgramme de lithium est encore facilement détectable.

On peut obtenir des résultats beaucoup plus intéressants en utilisant la seconde *méthode d'enregistrement des courants d'oxydation d'un amalgame* antérieurement formé dans la goutte pendante. Par cette méthode il est possible d'analyser seulement les ions qui forment avec le mercure des amalgames.

La solution est versée dans le vase (Fig. 1) et fortement agitée et en même temps électrolysée sous une tension constante; la goutte pendante étant la cathode. Les premiers essais ont démontrés, que — quant à la sensibilité — les résultats dépassent

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quelques centaines de fois la méthode polarographique. Comme exemple de la sensibilité de cette méthode il faut souligner que tous les réactifs de la meilleure pureté accessible sur le marché démontrent des impuretés considérables.

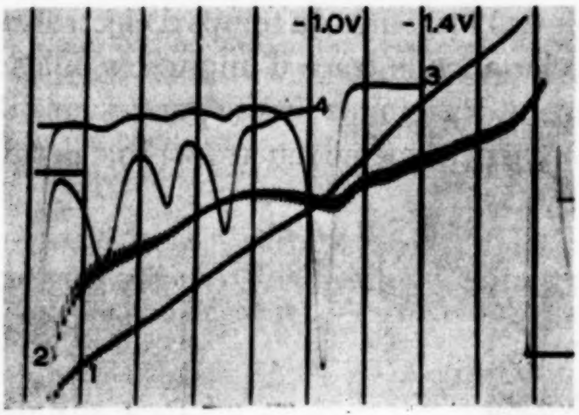

Fig. 5. La solution saturée de KCl pro analysi. Courbe 1: le polarogramme obtenu avec une sensibilité maximum du galvanomètre. Courbe 2: le même avec compensation. Courbe 3: oxydation d'amalgames après 2 min d'électrolyse sous le potentiel de —1.4 V. Courbe 4: le même après 15 min d'électrolyse sous le potentiel —1.0 V.

Les figures suivantes seront la meilleure preuve de l'efficacité de la méthode. La Fig. 5 donne un exemple d'analyse de la solution saturée de KCl, pro analysi deux fois cristallisée dans l'eau bidistillée. Le polarogramme (courbe 1) fait avec une électrode à gouttes sans compensation et avec une sensibilité maximum du galvanomètre montre une trace du zinc, à peine visible (courbe 2), si un polarogramme est fait avec une compensation du courant. Les courbes d'oxydation sont enregistrées après 2 min d'électrolyse (courbe 3) avec le potentiel —1.4 V et 15 min d'électrolyse avec le potentiel —1.0 V. On voit, qu'après 2 min le minimum, correspondant au courant d'oxydation du zinc, est grand; on peut déjà distinguer les minima correspondants au cadmium, plomb et cuivre. Ces minima sont beaucoup plus prononcés après 15 min d'électrolyse.

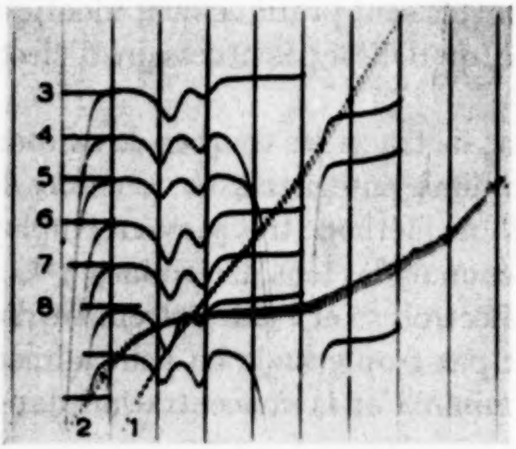

Fig. 6. La solution saturée de sulfate de potassium pro analysi. 1. Le polarogramme. 2. Le même avec compensation. Courbes 3, 4 et 5: oxydation d'amalgames après 10 min d'électrolyse sous le potentiel —1.0 et 1.4 V. Courbes 6, 7 et 8: le même — 20 min.

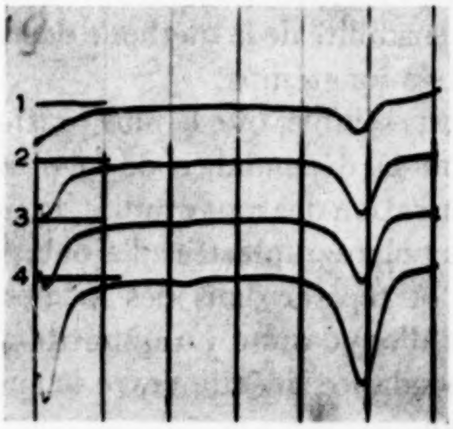

Fig. 7. La solution saturée de K_2SO_4 préalablement électrolysée. Courbes d'oxydation des amalgames: 1, après 5 min d'électrolyse: 2 et 3, après 10 min ; et 4, après 20 min d'électrolyse.

Passons à la solution saturée de sulfate de potassium pro analysi (Fig. 6). On ne peut pas remarquer sur des polarogrammes (courbes 1 et 2) des impuretés, mais les courbes

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d'oxydation, montrent de grandes quantités de zinc, et de petites quantités de cadmium et de plomb.

La même solution, électrolysée pendant 20 h pour éliminer les ions, contient seulement de petites quantités de zinc (Fig. 7).

La Fig. 8 est un exemple de l'influence du temps d'électrolyse. Dans ce cas les polarogrammes ne peuvent déceler aucune trace d'impuretés, mais les courbes d'oxydation démontrent l'agrandissement des minima, causé par des ions du plomb (courbes 1,2,3, faites après 3, 6 et 30 min). On peut même remarquer une petite trace des ions cadmium sur la courbe 5.

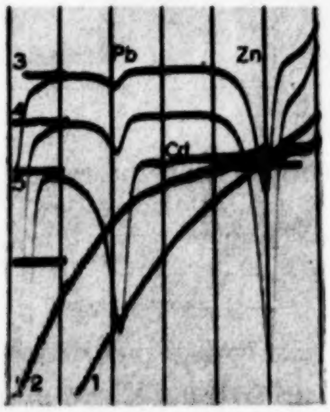

Fig. 8. La solution 0.1 *M* de K_2SO_4 pro analysi. 1. Le polarogramme; sensibilité demi-maximum du galvanomètre. 2. Le même avec compensation et sensibilité maximum. Courbes d'oxydation: 3, après 3 min; 4, après 6 min; et 5, après 30 min.

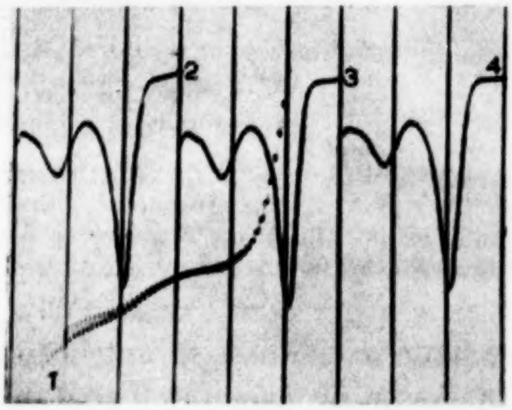

Fig. 9. La solution 0.1 *M* d'acide chlorhydrique pro analysi. 1. Le polarogramme avec compensation. 2. Courbe d'oxydation après 7 min d'électrolyse avec le potentiel —0,6 V. 3 et 4, le même sur d'autres gouttes.

Voici encore un exemple d'analyse d'acide chlorhydrique pro analysi (Fig. 9). Le polarogramme ne peut déceler les traces de plomb et de cuivre, dont les minima sont facilement enregistrés pendant l'oxydation d'un amalgame, après 7 min d'électrolyse. Trois courbes, enregistrées sur trois différentes gouttes sont pratiquement identiques.

La sensibilité de la méthode décrite est si grande, qu'il n'est pas nécessaire d'électrolyser très longtemps.

Il nous semble, que le plus pratique sera non pas de tracer les courbes de calibrage, donnant la dépendance de la profondeur des minima enregistrés en fonction de la concentration des ions étudiés, mais de se servir d'une méthode très souvent employée par les polarographistes: d'ajouter une quantité connue des ions déterminés à la solution et répéter dans des mêmes conditions l'électrolyse et l'enregistrement d'une courbe d'oxydation. La quantité ajoutée n'étant pas trop grande on peut admettre la dépendance linéaire entre la profondeur des minima et la concentration dans la solution.

En employant un galvanomètre de sensibilité 10^{-9} amp/mm/m, on peut évaluer les concentrations de l'ordre de 10^{-8} mole/l et même plus petites, en utilisant 3 à 15 ml de la solution. L'utilisation d'un galvanomètre encore plus sensible et d'un temps plus long d'électrolyse peut encore augmenter les limites de détection des ions.

Bien meilleure nous semble la méthode de la mesure de la quantité de coulombs qui ont traversé le circuit pendant l'oxydation d'un amalgame. Nous préparons maintenant la construction d'un tel appareil.

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RÉSUMÉ

Nous avons décrit l'application de la goutte pendante de mercure à l'analyse. Deux cas d'application de la méthode oscillopolarographique aux processus réversibles et irréversibles ont été présentés.

La méthode d'estimation de petites quantités d'ions aluminium, et de très petites (10^{-5} mole/l) d'ions lithium a été décrite.

En se servant d'un polarographe et d'un vase d'une construction simple on a montré la possibilité d'utilisation de l'électrolyse antérieure avec un courant continu conduisant à la formation d'un amalgame sur la goutte pendante. La méthode d'enregistrement du courant d'oxydation de cet amalgame est presentée. Cette méthode permet de déceler des concentrations de 10^{-8} mole/l des ions de Cu, Tl, Pb, Cd et Zn dans quelques ml de la solution analysée.

SUMMARY

The application of the hanging mercury drop electrode in analysis is described. Two cases of application of the oscillo-polarographic method to reversible and irreversible processes are presented.

A description is given of the method of estimating small quantities of aluminium and very small quantities (10^{-5} moles/l) of lithium.

Using a polarograph and a vessel of simple construction, the authors demonstrate the possibility of utilizing preliminary electrolysis with a continuous current, leading to the formation of an amalgam on the mercury drop. The method of registration of the oxydation current of this amalgam is presented. This method permits the detection of concentrations of 10^{-8} moles/l of Cu, Tl, Pb, Cd and Zn ions in a few ml of the solution analysed.

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CURRENT SCANNING POLAROGRAPHY AT THE DROPPING MERCURY ELECTRODE

by

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INTRODUCTION

During the course of a potentiometric study using the dropping mercury electrode at constant current, it became desirable to record current-scanning polarograms automatically. Recently, ADAMS, REILLEY AND FURMAN[1] introduced a manual method to obtain current-controlled polarograms at a platinum electrode. Their method, using a variable resistance inserted in series with the cell circuit to vary the current, could not be conveniently applied for our purpose because of the difficulty in scanning the current linearly. We[4] have developed a new method for obtaining current-scanning polarograms in which a high fixed resistance ($>$ 10 megohms) is used and the applied voltage is varied automatically from zero to 300 V. The characteristics of the polarogram obtained by this method are quite different from those observed in conventional polarography, especially since maxima do not appear on the current - potential curve. The limiting current, as defined in a subsequent section, is proportional to the concentration of electroactive species. Various interesting aspects of the new current-scanning method are described in the present paper.

INSTRUMENTATION

A diagram of the electrical circuit employed is shown in Fig. 1. The source of applied voltage is either a set of four 75-volt radio batteries or a 300-volt electronic rectifier (B in Fig. 1). The potential divider, P, is a 50,000 Ω wire resistance with a sliding contact driven by a synchronous motor. R is a standard resistance of 10 to 30 megohms. This circuit allows a controlled current of zero to 30 μA to flow through the electrolysis cell; the current does not vary with the cell resistance which is negligibly small in comparison with the value of R.

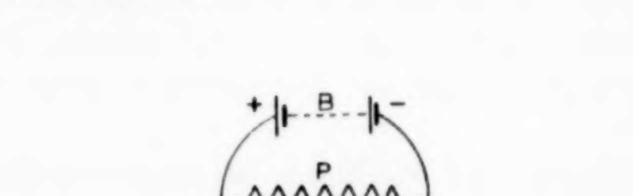

Fig. 1. Fundamental circuit of polarograph.

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An electronic balancing potentiometer recorder (Yanagimoto Co., Kyoto) was inserted in parallel with the electrolysis cell. This recorder has a maximum sensitivity of 0.2 mV/mm as a voltmeter and 0.002 μA/mm as a galvanometer. The travelling speed of the recording pen is 4 sec/20 cm (full scale) at zero damping. Since the applied voltage is varied linearly with time by the synchronous motor, the automatic instrument continuously records the variation of electrode potential with applied current, and hence with time.

RESULTS AND DISCUSSION

Influence of external resistance

If the resistance, R, in Fig. 1 is zero and the applied voltage is varied from zero to 2 V, the whole circuit becomes equivalent to the one introduced by HEYROVSKÝ AND SHIKATA[2]. When the potential of the reference electrode is kept constant during electrolysis (*e.g.*, when a saturated calomel electrode is used as the reference electrode), the applied voltage, V, is equal to the electrode potential, E (*cf.* Fig. 2-a'). Fig. 2-a is the ordinary polarogram obtained with a solution of oxygen in 0.005M potassium chloride.

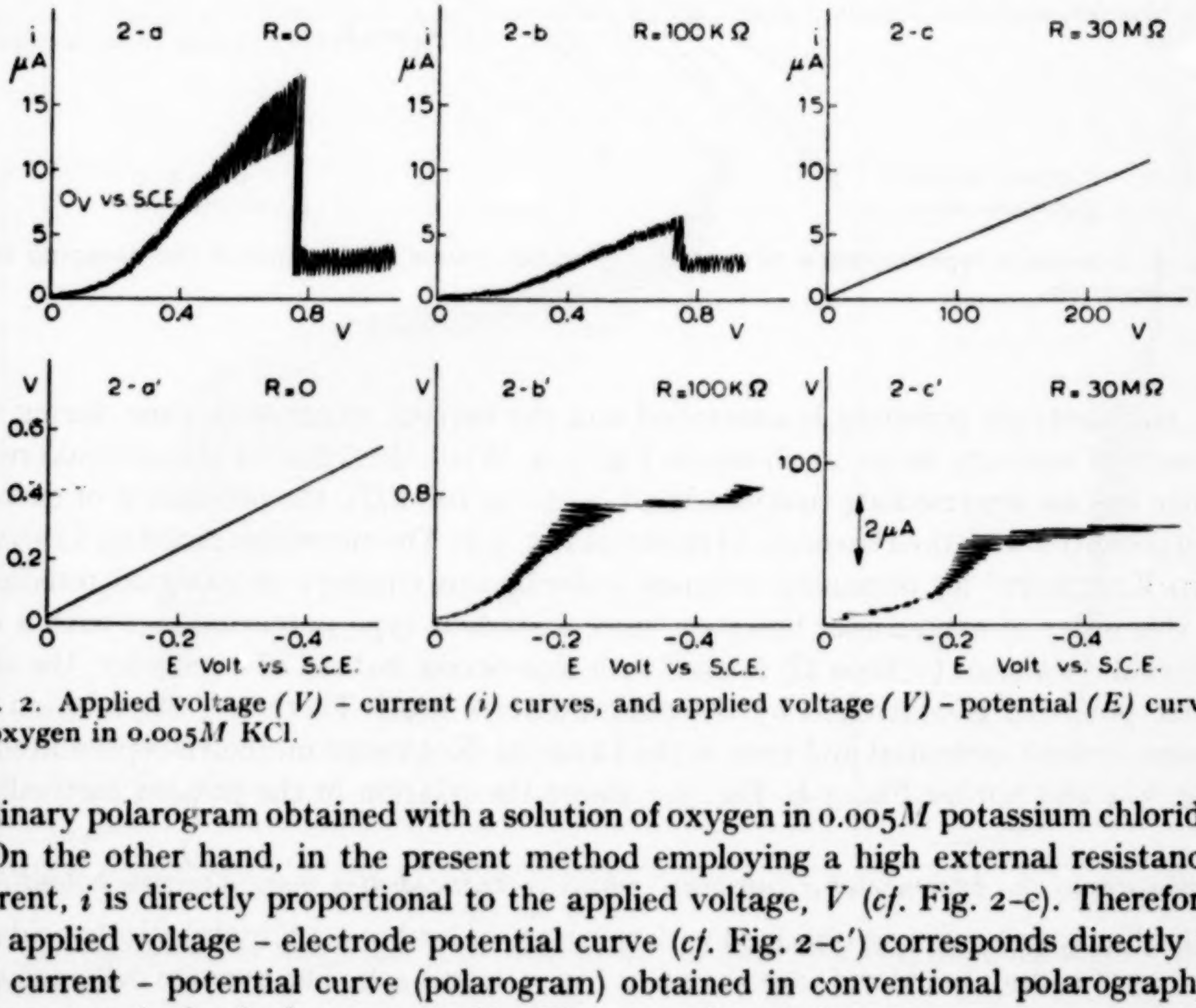

Fig. 2. Applied voltage *(V)* – current *(i)* curves, and applied voltage *(V)* – potential *(E)* curves of oxygen in 0.005M KCl.

On the other hand, in the present method employing a high external resistance, current, i is directly proportional to the applied voltage, V (*cf.* Fig. 2-c). Therefore, the applied voltage – electrode potential curve (*cf.* Fig. 2-c') corresponds directly to the current – potential curve (polarogram) obtained in conventional polarography. However, as is clearly demonstrated by Fig. 2-a and 2-c', these two curves are entirely different. No maxima appear in the curve obtained by the present method. Similarly, minima such as those observed on the nickel wave in a thiocyanate solution in conventional polarography do not appear on the $V(i) - E$ curve obtained by the present method. Fig. 2-b and 2-b' show the effect of an intermediate value for the external resistance.

Relations between current, potential and time with various values of external resistance can be schematically represented in Fig. 3. In conventional polarography ($R = 0$), the electrode potential is controlled and the current varies with time during the growth of mercury drops, as shown in Fig. 3-a. When the value of the external resistance has an intermediate magnitude (R = 10 to 100 kΩ), the oscillation of current and potential with time becomes as shown in Fig. 3-b. The circuit proposed by LINGANE AND KOLTHOFF[3] for obtaining ordinary polarograms employs an external resistance of this order of magnitude; however, since a student type potentiometer with a low internal resistance ($<1000\ \Omega$) is used with this circuit instead of a recorder, the electrode potential is controlled by the potentiometer itself. Therefore, the relation between current, potential and time in the LINGANE-KOLTHOFF method is represented by Fig. 3-a and not by Fig. 3-b. Fig. 3-c shows the relation in the present method[4].

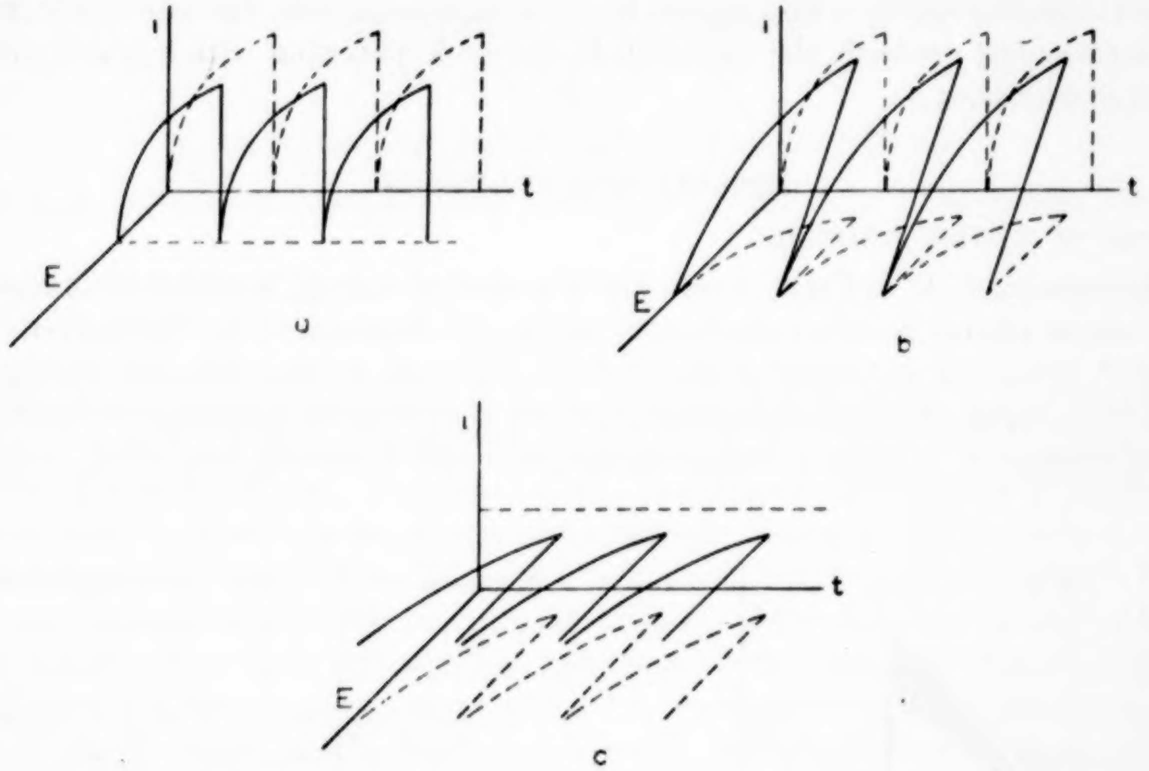

Fig. 3. Schematic representation of current – potential – time relationship at the dropping mercury electrode.

Influence of the presence of a substance which is reduced at a more negative potential

Ordinary polarograms obtained with solutions of lead in 0.1N hydrochloric acid and in 0.05M cadmium chloride are shown in Fig. 4-a and 4-b. The average diffusion current is practically the same in both cases. The polarograms obtained by the present method with the same solutions are shown in Fig. 5-a and 5-b. It is apparent that the oscillation of the electrode potential E during the life time of the mercury drop is greater in hydrochloric acid than in cadmium chloride solution. This phenomenon occurs because the current density is so large at the beginning of the drop growth that the potential of the mercury drop can be shifted to a negative potential where another

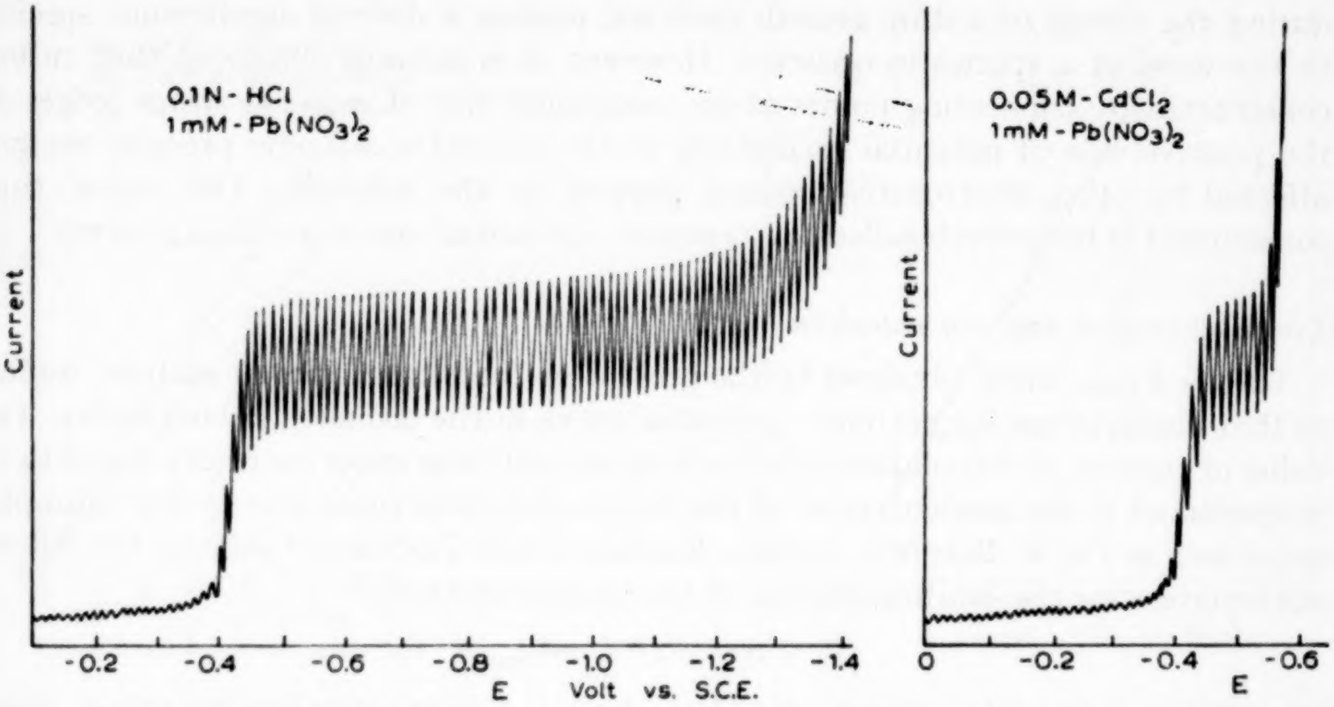

Fig. 4. Polarograms of lead ions in 0.1N hydrochloric acid and in 0.05M cadmium chloride (conventional polarography, HEYROVSKÝ AND SHIKATA).

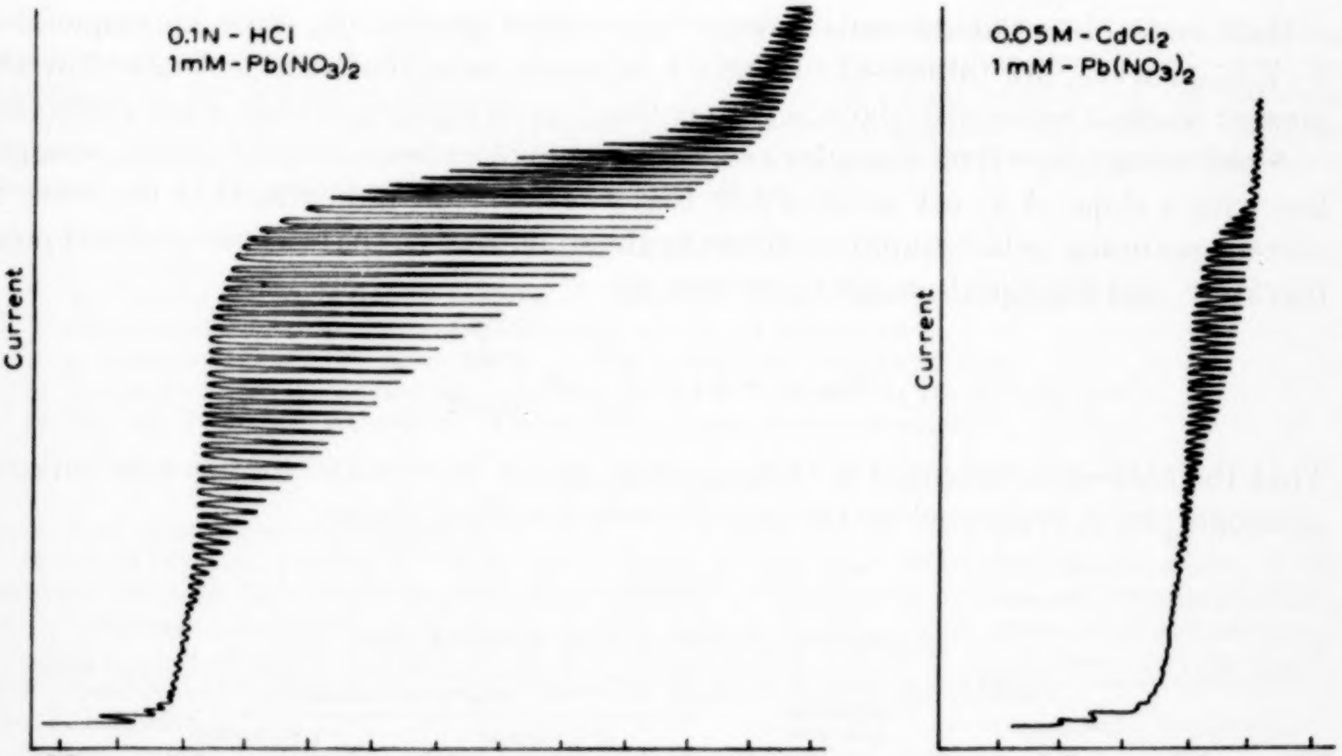

Fig. 5. Polarograms of lead ions in 0.1N hydrochloric acid and in 0.05M cadmium chloride (present method).

species is reduced. Therefore, the extent of this potential shift is dependent upon the species which is reduced at a more negative potential. Naturally, when the current is still small, the potential shift is not affected by the species which gives the next wave (*cf.* Fig. 5-a and 5-b).

It is clear from the above consideration that the oscillation of the electrode potential during the course of a drop growth does not possess a defined significance specific to the wave of a species in question. However, it is actually observed that curves constructed by connecting points at the maximum size of mercury drops (edges at the positive side of potential oscillations in the case of a cathodic process) are not affected by other electroactive species present in the solution. The curve thus constructed is henceforth called the "current - potential curve (i - $E_{\max}$ curve)".

Limiting current and concentration

The i - $E_{\max}$ curve obtained by the present method has a current plateau similar to that observed on the current - potential curve in the ordinary polarography. The value of current at this plateau (the limiting current) was experimentally found to be proportional to the concentration of the electro-reducible substance. A few examples are shown in Fig. 6. Recently, SENDA, KAMBARA AND TAKEMORI[5] derived the following equation for the limiting current of the present method:

$$i_1 = 635\, n\, D^{\frac{1}{2}}\, C\, m^{\frac{2}{3}}\, t_{\max}{}^{\frac{1}{6}}$$

where i_1 is expressed in microamp., D in cm/sec, C in m moles/l, m in mg/sec, and t in sec.

Half-wave potential and equation for the current-potential curve

Half-wave potentials of various ions, determined graphically from corresponding i - $E_{\max}$ curves, are tabulated in Table I. It can be seen that values obtained by the present method agree with those in conventional polarography within a few millivolts.

A plot of log $i/(i_1-i)$ *vs.* $E_{\max}$ for a solution of 1 mM lead in 0.1 N HCl yields a straight line with a slope of 37 mV as shown in Fig. 7. This result indicates that the wave in current-scanning polarography analyses in the same way as that in conventional polarography, and the equation can be written as:

$$E_{\max} = E_{\frac{1}{2}} - \frac{RT}{nF} \ln \frac{i}{(i_1-i)}$$

That the half-wave potential in this equation should be equal to that in conventional polarography is evidenced by the experiments described above.

TABLE I

HALF-WAVE POTENTIALS OF VARIOUS IONS

Ions	*Supporting electrolyte*	$E^1/_2$ *V vs. S.C.E.*	
		H.S. method	*I.F. method*
Pb^{+2}	0.1 M KCl	0.46_3	0.46_0
Cd^{+2}	0.1 N HCl	0.61_4	0.61_1
Cu^{+2}	1 M NH_3, NH_4Cl	0.53_2	0.53_3
Zn^{+2}	1 M NH_3, NH_4Cl	1.39	1.40

It should be emphasized that in the potentiometric titrations at constant current with a dropping mercury electrode, the potential to be measured should be the value at the maximum size of mercury drops, for this potential is not affected by other reducible substances present in the solution.

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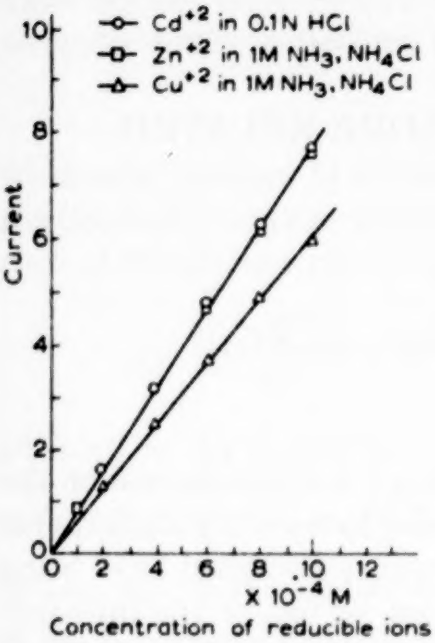

Fig. 6. Proportionality of limiting current to the concentration of reducible ion.

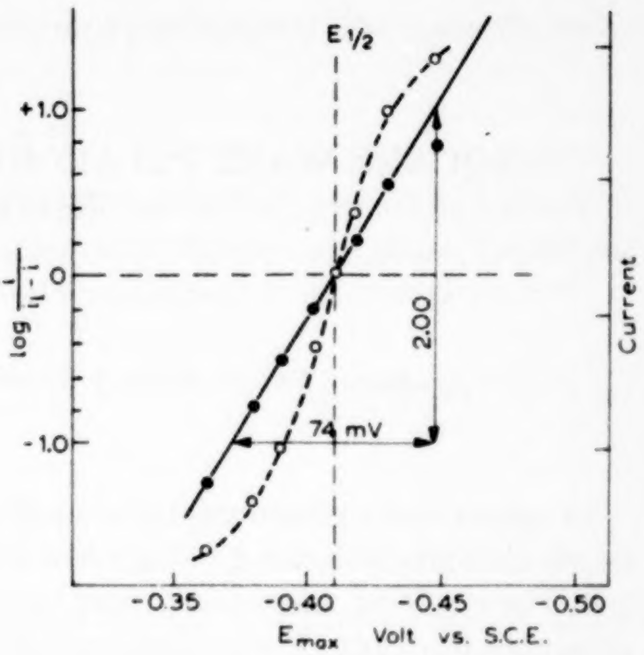

Fig. 7. Analysis of the wave of 1 mM lead ion in 0.1N hydrochloric acid.

SUMMARY

An instrumentation for obtaining current-scanning polarograms is proposed and the resulting polarograms are discussed. The proportionality of the limiting current to the concentration, the agreement of the half-wave potential with that of the ordinary polarography and the influence of external resistance on the relations between current, potential and time are described. In potentiometry at constant current with the dropping mercury electrode, the electrode potential should be measured at the maximum size of the mercury drops.

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DISCUSSION

Prof. I. M. Kolthoff (Minneapolis):

It seems that the potential – time curve should be the most interesting characteristic of the proposed method. Say, we are dealing with a solution of cadmium in a potassium chloride solution; one would expect during the early stages of formation of the drop a very negative potential corresponding to that of alkali amalgam in the later stages of the growth. It would seem that the potential – time curves constitute the real interesting characteristic of the method.

Dr. T. Fujinaga:

(I wish to thank Prof. Kolthoff for his kind interest and advice).

I hope we will be able to make a further study on the potential – time curve with an oscilloscope.

Prof. B. Breyer (Sydney):

A plot of log $i/i_1 - i$ *vs.* E with the solution of Pb^{+2} should show the slope of 30 mV.

Dr. T. Fujinaga:

Original polarographic wave was recorded by the automatic instrument, and the difference of 7 mV in slope might be due to the slow response of the recording pen.

SQUARE WAVE POLAROGRAPHY AND SOME RELATED TECHNIQUES

by

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Atomic Energy Research Establishment, Harwell, Berks. (England)

In square wave polarography[1] a small square wave voltage is superimposed on the slowly changing polarizing voltage which is applied to the electrodes of a polarographic cell. The resulting alternating component of the cell current is amplified after being separated from any slowly-changing diffusion current. Then, by means of a time-sensitive detector, an output voltage is derived which is proportional to the amplitude of this alternating current shortly before each change in the sign of the square wave voltage. Normally, the conductivity of the solution in the cell is sufficiently high to allow rapid charging and discharging of the double-layer capacity of the dropping mercury electrode, and the output voltage then should only be affected by periodic changes in the rates of electrode reactions produced by the square wave component of the drop potential. Usually the output voltage is not recorded continuously but, by means of a strobing circuit, a voltage equal to the output voltage of the detector at a definite time in the life of the mercury drop is fed to a pen recorder. The resulting strobe polarogram refers to an electrode of constant surface area.

With the original model of the square wave polarograph[1] reversibly-reduced ions could be detected at concentrations down to about $2 \cdot 10^{-7} M$. Subsequent improvements in circuit design (which have been incorporated in the instrument* which is commercially produced) have reduced this lower limit to about $4 \cdot 10^{-8} M$. The lower limit for irreversibly-reduced species is usually about $10^{-6} M$. The square wave frequency has been 225 c/s for all instruments so far constructed.

The analytical applications of the square wave polarograph have been mainly studied by MILNER and co-workers and a recent review[2] of this work indicates very clearly the advantages of the instrument over the conventional polarograph. It has been used for the analysis of metals, alloys, waters, effluents, fertilizers, food stuffs and in determinations of the age of minerals. In these applications the high sensitivity and resolving power of the instrument, combined with its ability to detect traces of reducible ions in the presence of a major constituent which is reduced at a more positive potential, has usually led to increased accuracy and to a decrease in the time needed to carry out a determination.

In the present paper the theory of square wave polarography is briefly reviewed, and ways of obtaining greater sensitivity and reproducibility in A.C. polarography are considered.

THEORY

To make full use of the information recorded on a square wave polarogram some knowledge of the theory of square wave polarography is essential. For a simple reversible electrode reaction, such as the reaction

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* Mervyn Instruments, Woking, England, Polarograph Type 1336 A.

$$O + n\varepsilon \rightleftharpoons R$$

when only reactant O is initially present in the solution and R, formed as a result of the electrode reaction, dissolves in either the solution or the mercury phase, the amplitude of the alternating component of the interfacial current density is given by[3]

$$i = \pm \frac{n^2F^2}{RT} C_\circ \triangle E \frac{P}{(1+P)^2} \sqrt{\frac{D_\circ}{\pi\tau}} \sum_{m=0}^{\infty} (-1)^m \frac{1}{\sqrt{m+\beta}} \text{ amp cm}^{-2} \quad . \; . \; . \; (1)$$

where $\beta = t/\tau \; (0<t<\tau)$

and $P = \exp{(E - E_{\frac{1}{2}})nF/RT}$.

In eqn. (1) t is the elapsed time (sec) since the last change in square wave sign, and τ is the half-period (sec) of the square wave voltage. E is the mean potential of the mercury drop and $E_{\frac{1}{2}}$ is the half-wave potential, whilst $\triangle E$ is the peak to peak amplitude of the square wave voltage. $C_\circ$ is the concentration (moles cm^{-3}) of O in the bulk of the solution and $D_\circ$ is the diffusion coefficient (cm^2 sec^{-1}) of O.

Eqn. (1) shows that a wave produced by a reversible reduction — a "reversible" wave — is symmetrical about the half wave potential and its maximum height is proportional to n^2 and to $D_\circ^{\frac{1}{2}}$. Although this equation is strictly valid only for $\triangle E \ll \frac{RT}{nF}$, it is sufficiently exact for most analytical purposes. For small $\triangle E$ the width of a "reversible" wave at half its maximum height (the half-wave width) at 25°C is 90.4 and 45.2 mV, respectively, for $n = 1$ and $n = 2$.

If the electrode reaction is slightly irreversible, but not so irreversible that the variation of the mean concentration of O at the electrode surface with E is appreciably affected, the appropriate expression[3] for i is

$$i \simeq \pm \frac{n^2F^2}{RT} C_\circ \triangle E \frac{k_{\frac{1}{2}}}{(P^{-\alpha_2} + P^{\alpha_1})} \sum_{m=0}^{\infty} (-1)^m \exp M^2(m+\beta) \operatorname{erfc} M \sqrt{m+\beta} \text{ amp cm}^{-2} \quad (2)$$

where $M = (P^{-\alpha_1} + P^{\alpha_2})k_{\frac{1}{2}} \sqrt{\frac{\tau}{D_\circ}}$

and $k_{\frac{1}{2}}$ is the rate constant (cm sec^{-1}) of the forward electrode process (the reduction of O) at $E = E_{\frac{1}{2}}$, whilst α_1 and α_2 represent the transfer coefficients of the forward and reverse processes, respectively. Slight irreversibility does not greatly affect the symmetry of the wave and, for $\alpha_1 = \alpha_2 = 0.5$, the irreversibility reduces i by less than 2% if $M \geq 10$.

In the case of a semi-irreversible reaction, when both electrode processes still make a contribution to the wave but the variation of the mean concentration of O at the electrode surface with E is influenced by the irreversibility, the expression for i takes its most general form[4],

$$i = \pm \frac{n^2F^2}{RT} \triangle E \, (\alpha_1 k_f C_\circ^\circ + \alpha_2 k_b C_r^\circ) \sum_{m=0}^{\infty} (-1)^m \exp N^2(m+\beta) \operatorname{erfc} N \sqrt{m+\beta} \text{ amp cm}^{-2} \, (3)$$

where C_r°, the concentration of R at the interface is given by $C_r^\circ = D_o^{\frac{1}{2}}/D_r^{\frac{1}{2}}\,(C_o - C_o^\circ)$ in the case in which R is only present as a result of the electrode reaction. C_o°, the concentration of O at the electrode surface, varies with the age of the mercury drop, but can be evaluated with the aid of an equation derived by KOUTECKY[5]. The parameter N in eqn. (3) is defined by the equation

$$N = (k_f/D_o^{\frac{1}{2}} + k_b/D_r^{\frac{1}{2}})\tau^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots \quad (4)$$

In eqns. (3) and (4) k_f and k_b, respectively, are the rate constants of the forward and reverse processes of the reaction, and D_r is the diffusion coefficient of R in the phase in which it dissolves.

Eqn. (4) is not of much practical value but it is the only equation which can account for the shape of an asymmetric wave such as that produced by the reduction of zinc ion in chloride, perchlorate and other media.

If the reaction is totally irreversible eqn. (3) takes the simpler form[3]

$$i = \pm \frac{n^2F^2}{RT} \Delta E a_1\, C_o^\circ\, k_f \sum_{m=0}^{\infty} (-1)^m \exp N^2 (m+\beta)\, \mathrm{erfc}\, N\sqrt{m+\beta} \text{ amp cm}^{-2} \quad (3a)$$

where $N = k_f \sqrt{\dfrac{\tau}{D_o}}$

Again C_o° can be evaluated with the aid of Koutecky's equation, and one then finds[3] that a "totally irreversible" wave is almost symmetrical but its maximum height is of the order of twenty times smaller than for a completely reversible reduction, (when measurements are made at a time about 2 sec after the fall of the previous drop and $\tau = 2.2$ msec). The half wave width is considerably increased and hence there is some danger of confusing a "totally irreversible" wave associated with an n value of 2 with a "reversible" wave produced by a reaction for which n equals 1.

The validity of eqns. (1), (2), (3) and (3a) has been tested[6] and agreement between theory and experiment has been found in all cases in which the reaction rate is either completely diffusion controlled or controlled partly by diffusion and partly by the irreversibility of a simple electrode reaction. Some difference between theory and experiment has been observed in a number of highly irreversible reductions. In these cases — the reduction of the ions of iron, cobalt and nickel, — the discrepancy is believed to be due to the existence of consecutive rate-controlling processes, one of which may be the partial dehydration of the hydrated metallic ion as it enters the double-layer.

METHODS FOR OBTAINING INCREASED SENSITIVITY

The maximum sensitivity which can be obtained by the square wave method is usually limited, not by the noise level of the electronic circuits (as it ideally should be), but by the instability of a response associated with a tendency for solution to enter the capillary of the dropping mercury electrode. A thin film of solution surrounds the lower part of the mercury thread within the capillary and makes it possible for the surface of the mercury thread to slowly follow changes in drop potential. The aperiodic equivalent circuit for the polarographic cell in the absence of reducible ions (Fig. 1) then consists not merely of a resistance in series with the double-layer capacity of the mercury drop, but has an additional circuit component which shunts the double-layer capacity and takes the form of a tapering resistive transmission line. The taper is connected with the fact that the liquid film decreases in thickness as the distance from the capillary tip increases. If the potential of the dropping mercury electrode is suddenly changed there is a small current which decays slowly with time (the capillary response) as well as a much larger rapidly-decaying current associated with the charging of the double-layer capacity of the surface of the mercury drop. The capillary response generally decays according to a power of t smaller than $-\frac{1}{2}$ because of the taper mentioned above, and since, in the case of a reversible electrode reaction, the corresponding change in reaction rate[3] decays according to $t^{-\frac{1}{2}}$, it is evident that for a high ratio of electrode reaction response to capillary response in A.C. polarography, the frequency should be as low as possible. Experience has shown that a square wave frequency of 225 c/s, while advantageous as regards the elimination of spurious responses associated with vibration of the drop, does not lead to the best results in low level determinations. At maximum sensitivity, the baseline of the square wave polarogram tends to rise on either side of the potential of the electro-capillary maximum, the rise being particularly marked at positive potentials. These changes in baseline level are partly caused by variations in the thickness of the liquid film and they are clearly undesirable since they make it difficult to measure the height of a small wave. Also, as the capillary response tends to vary slightly from drop to drop, the noise level of the strobe polarogram is increased and may be as much as four times larger than that attributable to noise in the electronic circuits.

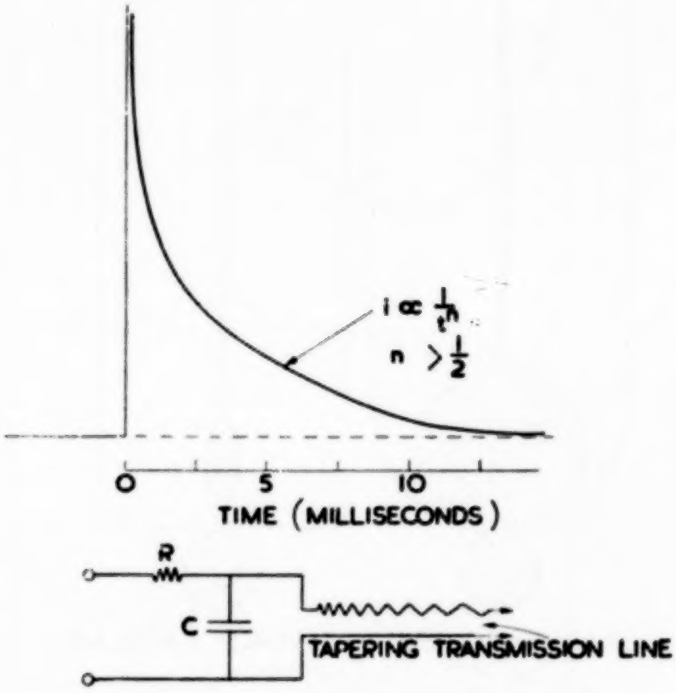

Fig. 1. Equivalent circuit of cell and decay of capillary response following a change of drop potential.

The capillary response can be made more stable by using capillaries of special design, such as the tapered and bulb capillaries shown in Fig. 2. Of these, the latter type is more easy to construct and can be made by applying compressed air to one end of a short length of 0.05 or 0.1 mm bore capillary tubing while the other end of the tubing is rotated in a hot flame. With such capillaries the short term fluctuations in the capillary response usually are largely eliminated and the polarograms are much more reproducible (Fig. 3). Also one can reduce both the capillary response and the short term variations in capillary response by water-proofing the tip of a conventional capillary with a silicone resin (Fig. 3). Water-proofed capillaries, however, are not suitable for use with acid solutions at potentials more negative than about —0.9 V *vs.* S.C.E.

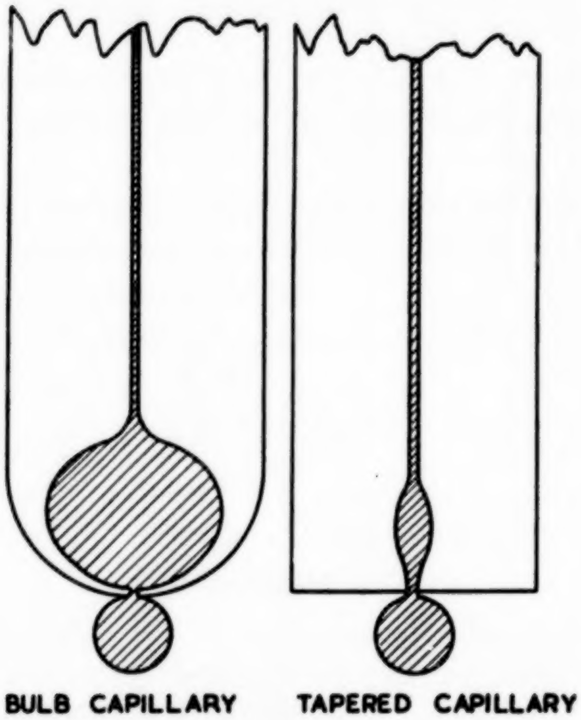

Fig. 2. Bulb and tapered capillaries.

Although the measures mentioned above may produce some improvement in sensitivity none of them can be considered entirely acceptable for use in routine analysis and we have sought other methods for obtaining increased sensitivity.

One method for eliminating errors arising from drop-to-drop fluctuations in the capillary response involves the use of a rapid synchronised potential sweep[7] (such as is used in cathode ray polarography) combined with a high-speed recorder or cathode-ray tube presentation. By this method, with a modified square wave polarograph, we have been able to detect reversibly-reduced ions at concentrations below $10^{-8}M$ without loss of resolving power and without seriously impairing the ability of the instrument to discriminate against interfering ions.

Yet another method for obtaining increased sensitivity makes use of a sessile mercury drop[8] as an electrode. Before a square wave polarogram is recorded, the drop is polarized for some time in a stirred or unstirred solution at such a potential that traces of metallic ions in the solution are concentrated in the drop. When recording a polarogram, one starts at the potential chosen for ion concentration and makes the drop potential become more positive as time progresses. Although, in favourable circumstances, this technique can be used for the detection of metallic ions at concentrations below $10^{-9}M$, it is of limited application because of difficulties associated with the poisoning of the electrode surface by traces of organic matter in the solution. To obtain the sessile drop polarograms shown in Fig. 4, the base solution was pre-electrolysed and treated with charcoal to remove some inorganic (Cu, Pb, Cd) and most

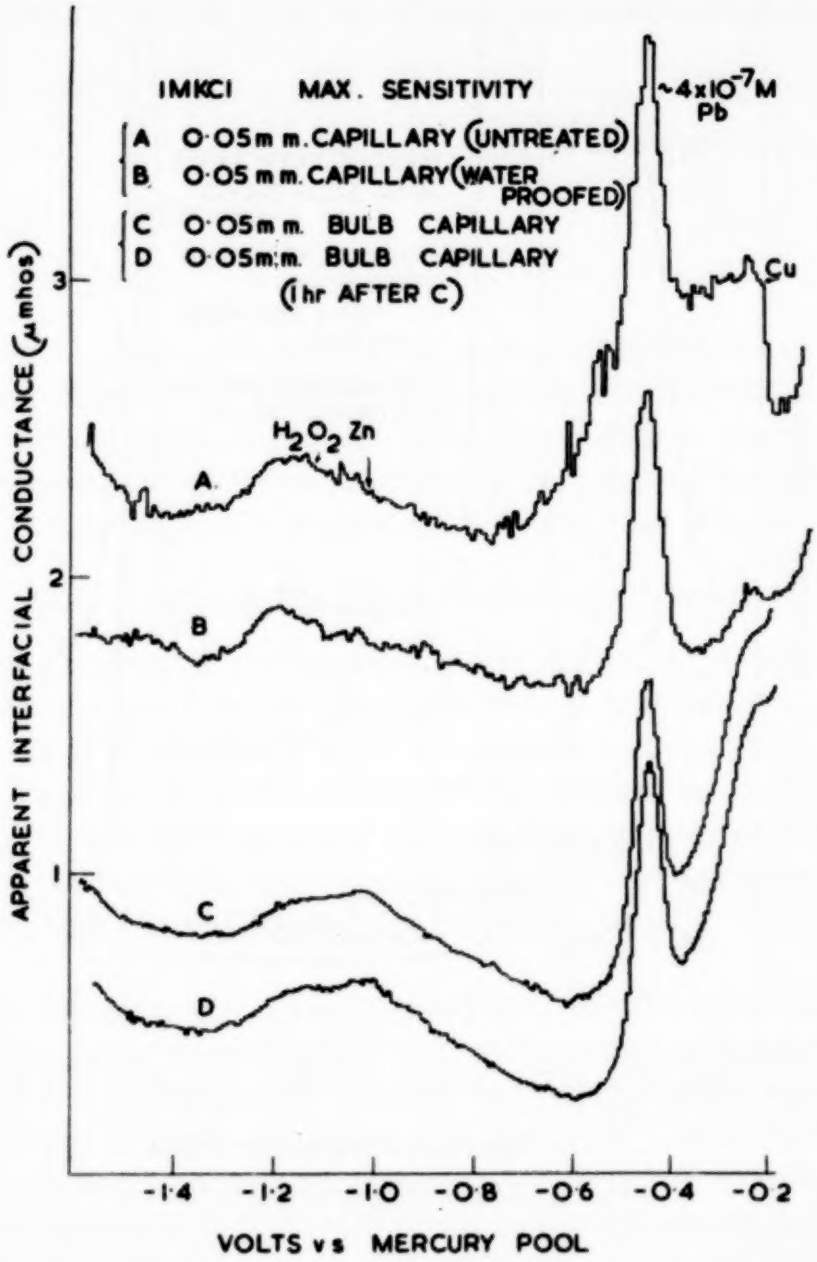

Fig. 3. Square wave polarograms for different types of capillary.

organic impurities, and the sample of "Specpure" KCl was roasted to destroy organic matter.

A third method for obtaining increased sensitivity in A.C. polarography, which will be described more fully elsewhere, makes use of a polarizing pulse with a duration of 1/25 sec that is applied to the dropping mercury electrode, once in the life of each drop and at a definite time in the drop-life. A new instrument, the pulse polarograph[9], has been developed, which uses this pulse technique and gives not only a derivative polarogram, but also a normal polarogram of high sensitivity that is automatically compensated for diffusion current at the start of the polarogram. With the derivative circuit of this instrument reversibly-reduced ions can be detected at concentrations down to about $10^{-8}M$ and, because of the extended time scale (as compared with the square wave polarograph), the capillary response is comparatively small. Also, partly because of the change in time scale, the instrument is about 12 times more sensitive than the square wave polarograph as regards the determination of irreversibly-reduced ions. The pulse polarograph can be used with quite dilute base solutions ($0.01M$ KCl),

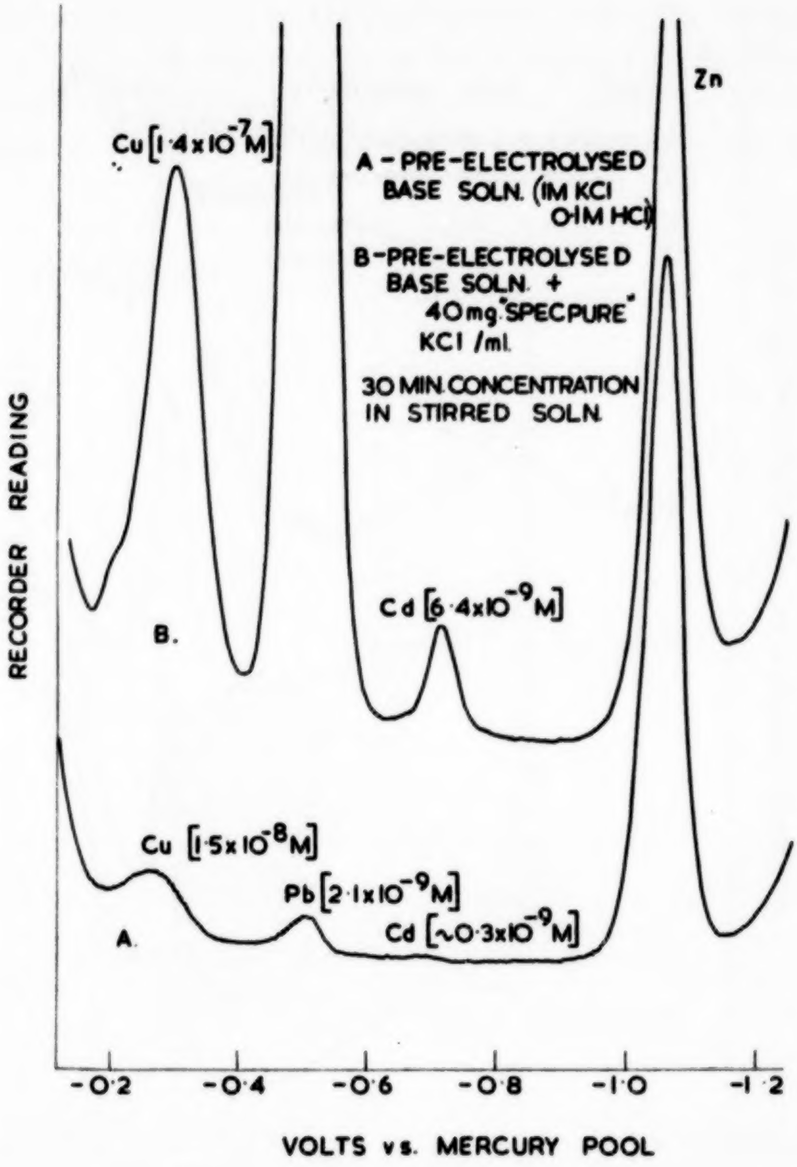

Fig. 4. Sessile drop polarograms.

whereas the square wave polarograph cannot generally be used with base solutions more dilute than 0.2*M*. At the present time it appears to be the most sensitive of existing A.C. polarographs, but there is reason to believe that the square wave polarograph will regain its supremacy when the R.F. technique mentioned in the next section is fully developed.

FARADAIC RECTIFICATION AND R.F. POLAROGRAPHY

The rectification of alternating current by electrodes has been recognised for many years. Usually it is connected with the passivation of an electrode when the current is flowing in one direction. There is, however, a type of rectification, recently termed faradaic rectification[10], which is observed when the amplitude of the alternating component of the interfacial potential is quite small (<10 mV). This rectification is caused by the non-linearity of electrode processes as regards the variation of their rates with potential. In the case of a mercury electrode and the reaction

$$O + n\varepsilon \rightleftharpoons R$$

when O is present in the solution and R is also present (in either the aqueous phase, or the mercury phase), it can be shown that if the electrode at equilibrium is polarized by a sinusoidal alternating current there is a change in mean electrode potential given by[4]

$$\boldsymbol{\Psi} = V^2 \frac{nF}{RT}\left[\frac{2a_1 - 1}{4} + \left(\frac{(1-a_1)\sqrt{D_o}C_o - a_1\sqrt{D_r}C_r}{2C_r\sqrt{D_r} + 2C_o\sqrt{D_o}}\right)\left(\frac{Z(k_e + \sqrt{2k_e^2Z})}{\sqrt{2}\,(1 + \sqrt{2k_eZ} + k_e^2Z^2)}\right)\right] \quad (5)$$

where $Z = \dfrac{C_r\sqrt{D_r} + C_o\sqrt{D_o}}{C_r\sqrt{\omega D_o D_r}}$

In eqn. (5) C_r and C_o, respectively, are the bulk concentrations of R and O, whilst D_r and D_o are their diffusion coefficients. V is the amplitude of the (almost sinusoidal) alternating component of the interfacial potential and ω is the angular frequency. The transfer coefficient of the forward process is represented by a_1 and k_e is the rate constant of this process when the system is at equilibrium. The above equation only holds for $V \ll \frac{RT}{nF}$ and, therefore, the observed potential change on applying the alternating polarizing current in an experiment test of eqn. (5) is quite small.

The most important point about eqn. (5) is that $\boldsymbol{\Psi}$ is dependent on a_1 and k_e and, by studying the effect of frequency on $\boldsymbol{\Psi}$ for various values of C_r/C_o, it is possible to determine both k_e and a_1. Recently, OLDHAM[10] has derived an expression for $\boldsymbol{\Psi}$ which differs from eqn. (5), but his theoretical treatment appears to be unsound and is certainly not in agreement with the experimental facts at very high frequencies. A solution derived earlier by DOSS AND AGARWAL[11] for the special case $C_o = C_r$, $D_o = D_r$ appears to be correct.

The faradaic rectification effect can be used to study the kinetics of electrode processes which are too rapid to be studied by the conventional faradaic impedance method[12]. In practice it is convenient to measure not the change in mean potential when an alternating current is applied to a mercury electrode, but the alternating current which has to be supplied to a dropping mercury electrode to keep its mean potential constant when the electrode is polarized by an amplitude-modulated radio-frequency current. We have used 225 c/s square wave modulation, and the low frequency alternating current produced by faradaic rectification at constant mean potential has been measured with a square wave polarograph, using the circuit shown schematically in Fig. 5. Radio-frequencies within the range 100 kc/s to 6.4 mc/s are used. The solution in the cell need only contain reactant O, the other reactant being formed in situ by the reduction of O at the electrode surface. The ratio of the concentrations of the two reactants at the electrode surface is varied by changing the mean potential of the dropping mercury electrode. As in square wave polarography, the variation of the output voltage of the time-sensitive detector at a definite time in the life of each drop

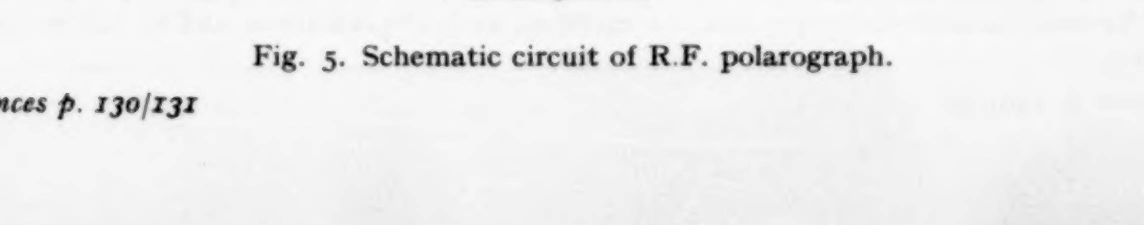

Fig. 5. Schematic circuit of R.F. polarograph.

is recorded as E slowly changes. The wave which then appears on the recorder chart is termed a faradaic rectification wave.

In the case of a simple rapid reaction* one finds that the faradaic rectification current when only reactant O is present in the bulk of the solution, produced by a square wave — modulated R.F. current (100% modulation), is virtually the same as the alternating current produced in square wave polarography by a square wave — polarizing voltage with a peak to peak amplitude $\triangle E$ given by[6]

$$\triangle E = \frac{(1-2a_1)P^{2a_1}X^2 + \sqrt{2}P^{a_1}(1-a_1-a_1P)X + 1 - P^2}{4[P^{2a_1}X^2 + \sqrt{2}P^{a_1}(1+P)X + (1+P)^2]} \cdot \frac{V^2nF}{RT} \quad \ldots (6)$$

where $X = \sqrt{\omega D_{\circ}}/k_{\circ}$, $P = \exp(E - E_{\frac{1}{2}})\, nF/RT$, V is the amplitude of the alternating component of the interfacial potential, and $k_{\circ}$ is the rate constant of the forward electrode process at the potential at which the rate constants of the forward and reverse processes are equal. $\triangle E$ may be positive or negative in sign.

Theory[4] and experiment show that the double-layer capacity in the case of concentrated solutions is almost independent of frequency for frequencies up to 6.4 mc/s, and therefore, it is convenient to use low concentrations of the reducible ion ($<10^{-4}M$). Then, for $\omega > 2\pi \cdot 10^5$, the interfacial impedance at constant potential is controlled entirely by the double-layer capacity. In such circumstances, it is relatively easy to calculate the variation of V with mean potential and ω, if the R.F. current density, and the dependence of the double-layer capacity on the potential are known.

Fig. 6 shows the theoretical [eqns. (1) and (6)] variation with P of a quantity proportional to the height of the faradaic rectification wave for a rapid reaction when V is constant. The figure shows the effect of the parameter X on wave shape for three values of a_1. The wave has a second derivative shape at all frequencies if $a_1 = 0.5$ and its amplitude decreases with increasing frequency. If, however, the transfer coefficient is either smaller or larger than 0.5, the wave tends to assume the shape of a first derivative wave as the frequency increases, and its sign then depends on whether or not a_1 is greater than 0.5. In all cases the wave height, for constant V, as the frequency increases tends towards a limiting value proportional to $(1-2a_1)$. By studying the variation of wave shape and height with frequency a_1 and $k_{\circ}$ can be determined if $D_{\circ}$ is known. Some results obtained in this way** are given in Table I.

These are only preliminary results and it is expected that more accurate values of a_1 and $k_{\circ}$, will be obtained in the future. For the reduction of cadmium ion in 0.5M sulphate solution, the values of a_1 and $k_{\circ}$ are in fair agreement with values obtained by GERISCHER[13,14]. This particular reaction, which is generally regarded as a rapid reaction, appears to be a relatively slow reaction when the R.F. technique is used, and at the lowest frequency (100 kc/s) the wave has almost the shape of a first derivative wave.

Turning now to the use of this R.F. technique in polarographic analysis, one can see that because the capillary response in square wave polarography is produced by relatively linear components, these will have little effect on the R.F. polarogram. There is, however, an additional reason why the capillary response should disappear, connected

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* A reaction which appears to be reversible when studied with the square wave polarograph.

** The experimental technique and the methods used to evaluate a_1 and $k_{\circ}$ will be described elsewhere.

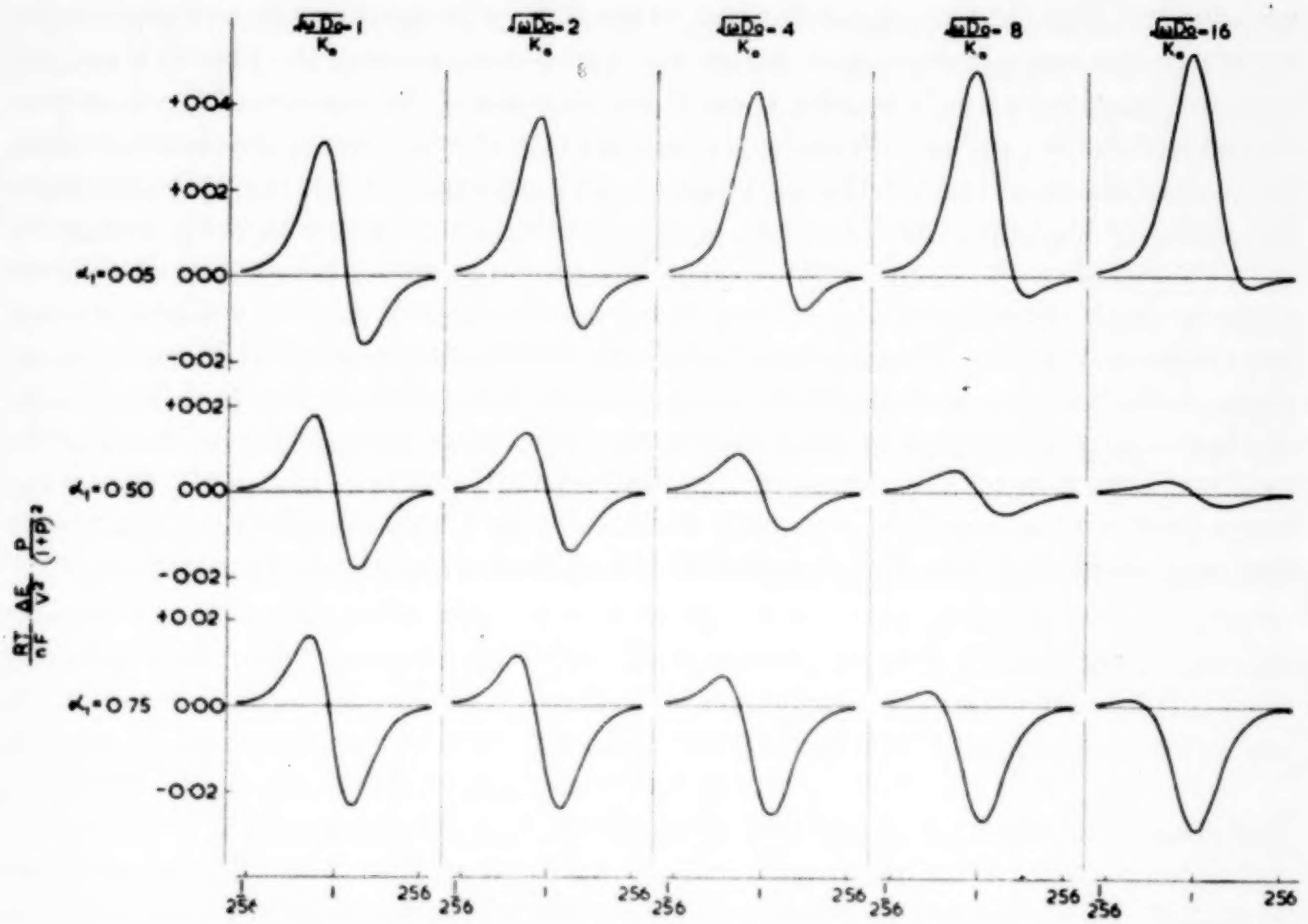

Fig. 6. Variation of faradaic rectification wave with a_1 and $\sqrt{\omega D_\circ}/k_\circ$.

TABLE I

APPROXIMATE VALUES OF a_1 AND $k_\circ$ AT 22°C

Base solution	*Reaction*	α_1	$k_\circ$ (cm sec⁻¹)
0.5M K_2SO_4	$Cd^{+2} + 2\varepsilon \rightleftharpoons Cd$	0.08	∼0.08
1M $NaClO_4$ (pH 2)	$Pb^{+2} + 2\varepsilon \rightleftharpoons Pb$	0.60	3.3
	$Cd^{+2} + 2\varepsilon \rightleftharpoons Cd$	0.07	2.3
	$UO_2^{+2} + \varepsilon \rightleftharpoons UO_2^{+}$	∼0.5	
1M KNO_3 (pH 2)	$Pb^{+2} + 2\varepsilon \rightleftharpoons Pb$	0.81	0.8
	$Cd^{+2} + 2\varepsilon \rightleftharpoons Cd$	0.15	6.3
1M $HClO_4$	$Pb^{+2} + 2\varepsilon \rightleftharpoons Pb$	∼0.51	∼3.6
	$Cd^{+2} + 2\varepsilon \rightleftharpoons Cd$	∼0.08	∼1.8
1M KCl (pH 2)	$Pb^{+2} + 2\varepsilon \rightleftharpoons Pb$	0.94	∼0.2
	$Cd^{+2} + 2\varepsilon \rightleftharpoons Cd$	0.78	2.9
	$Cu^{+} + \varepsilon \rightleftharpoons Cu$	>0.5	
	$Tl^{+} + \varepsilon \rightleftharpoons Tl$	∼0.9	∼0.15
	$In^{+3} + 3\varepsilon \rightleftharpoons In$	>0.18	<1.5
1M KCl 0.5M HCl	$UO_2^{+2} + \varepsilon \rightleftharpoons UO_2^{+}$	∼0.5	∼2.5

with the fact that the response in the case of the R.F. polarogram is proportional to the square of the voltage developed across the non-linear component. This voltage, at high frequencies, is much smaller than V for all parts of the surface of the mercury thread within the capillary. Microscopic defects in the dropping mercury electrode thus have virtually no effect on the polarogram, and polarograms for the same solution but different capillaries are identical, if the capillaries are macroscopically identical.

In studies of electrode processes, V usually does not exceed 5 mV, but in analytical work to obtain high sensitivity V may be increased to 25 mV or more without serious loss of resolving power. Though eqn. (6) does not hold for large values of V, wave shape varies with X and a_1 in roughly the same manner as is shown in Fig. 6. A frequency of about 400 kc/s appears suitable as the waves produced by many ions in chloride solutions then approximate in shape to a first derivative wave. The use of frequencies much greater than 400 kc/s, is usually undesirable as it may introduce a background response connected with R.F. heating of the solution surrounding the mercury drop.

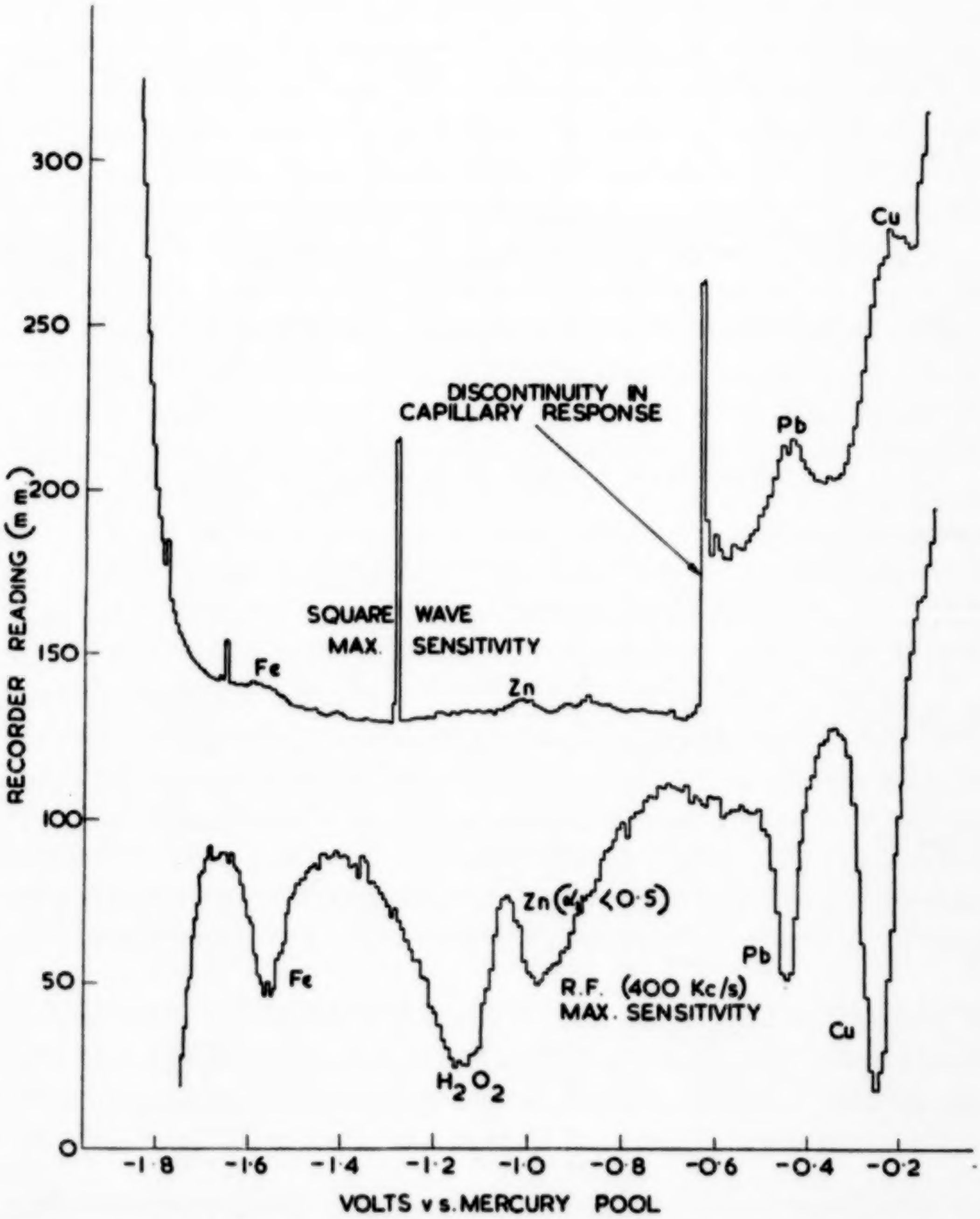

Fig. 7. Square wave and R.F. polarograms for a 1 M KCl solution containing traces of Cu, Pb, Zn, H_2O_2 and Fe.

Usually for reversibly-reduced ions, there is some loss of signal relative to the normal square wave polarograph. However, the signal/noise ratio is improved by the elimination of capillary response noise, and after increasing the gain of the electronic circuits there is usually at least a two-fold increase in sensitivity (Fig. 7) for reversibly-reduced ions. The gain in sensitivity for ions which are irreversibly reduced at potentials considerably more negative than the potential of the electro-capillary maximum is even greater (Fig. 7), owing partly to the decrease in double-layer capacity at such potentials and the concomitant increase in V. At the present time reversibly-reduced metallic ions can be detected at concentrations down to about $2 \cdot 10^{-8} M$ whilst many irreversibly-reduced ions can be detected at the $10^{-7} M$ level. The most striking feature of the low level R.F. polarogram, however, is its high degree of reproducibility. One expects that considerably higher sensitivity will be obtained in the future by using electronic circuits of lower noise level.

Table I shows that the rate constants and transfer coefficients of rapid electrode reactions vary considerably with the composition of the base solution. It is, therefore, probable that future work will show that the sensitivity of an R.F. polarograph for one ion relative to another can be controlled by changing the composition of the base solution. This feature of the R.F. technique clearly might facilitate the determination of species which cannot be resolved by other means.

One other advantage of the R.F. technique is that the surface area of th eanode of the polarograph cell can often be much smaller than in square wave polarography, and, consequently, polarographic cells of smaller volume can be employed. Also, it is possible in some cases to use a mercury meniscus in a capillary tube as the cathode of the polarographic cell. The use of such an electrode in square wave polarography does not give very high sensitivity due to the exceptionally large capillary response associated with this type of electrode. This response, however, is eliminated in R.F. polarography and it is possible to use a micro-cell of the type indicated in Fig. 8 which may contain as little as 0.01 ml of solution. The solution, with this design of cell, is trapped between a mercury meniscus with a surface area of about 0.01 cm^2 and a small mercury anode of somewhat larger surface area. A typical R.F. polarogram obtained with such a micro-cell is shown in Fig. 8. This type of cell can only be employed with solutions which are relatively free from organic matter, but it is clear that it may prove useful in the atomic energy field for the analysis of highly active solutions. Sensitivity is not greatly affected by the use of a meniscus electrode in place of the dropping mercury electrode and quantities of metallic ions as small as 10^{-10} g can be easily detected.

Although the R.F. technique is still relatively new, it appears to be potentially almost as important an advance as the square wave technique. It is clear, however, that its use demands a greater understanding of the kinetics of electrode processes than is needed in square wave polarography and hence it may be some time before it is accepted by analytical chemists.

To conclude, mention may be made of yet another technique which is a logical extension of the R.F. technique, and which makes use of a frequency-modulated current in place of an amplitude-modulated current. As in R.F. polarography, square wave modulation can most conveniently be employed and the frequency may be varied by a factor of 4 or more. The circuit used must be such that the alternating voltage developed across the double-layer capacity of the dropping mercury electrode is not am-

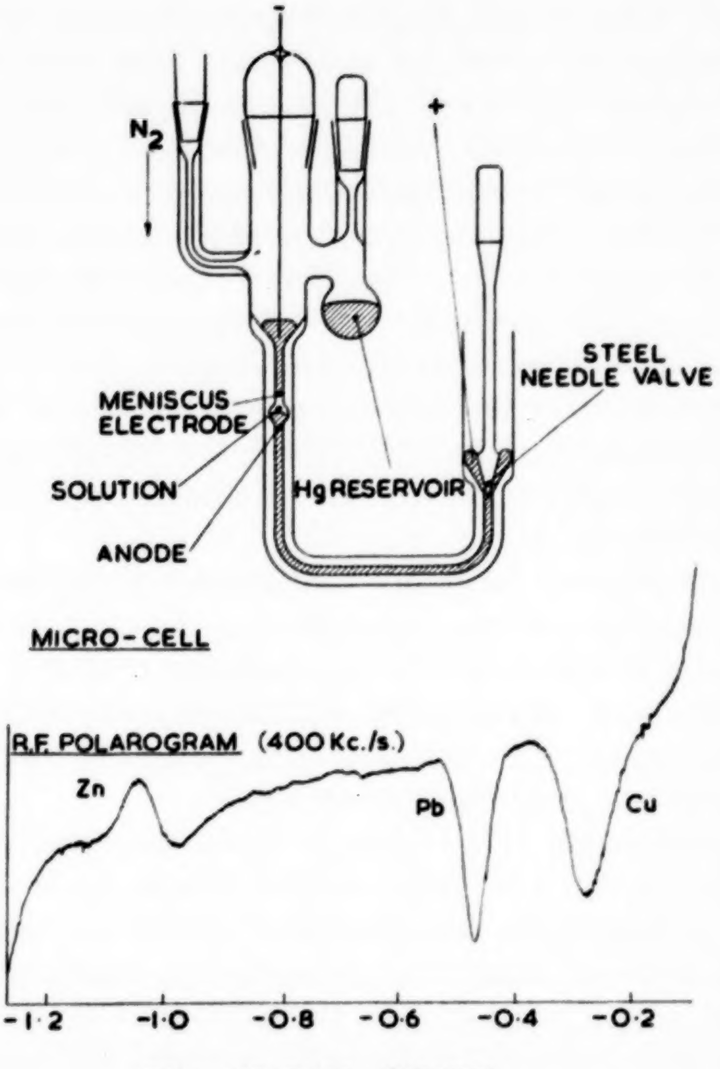

Fig. 8. Micro-cell and R.F. polarogram for $\sim 10^{-2}$ ml of acidified $2M$ KCl containing $\sim 10^{-9}$ g Pb, $\sim 1.5 \cdot 10^{-9}$ g Cu and $\sim 0.8 \cdot 10^{-10}$ g Zn.

plitude-modulated. The principal merit of this type of polarizing current is that the frequency modulation does not affect very reversible or totally irreversible reactions and by varying the frequency one can, so to speak, "tune in" slightly irreversible reactions having different k_0 values. Traces of metallic ions in solutions which have not been deoxygenated can be determined using this technique, because of the irreversibility of the processes involved in the reduction of oxygen and hydrogen peroxide.

SUMMARY

The theory of square wave polarography is reviewed, and methods for obtaining increased sensitivity in A.C. polarography are outlined, including a new technique which makes use of an amplitude-modulated radio-frequency polarizing current. This R.F. technique can also be used to study the kinetics of very rapid electrode processes.

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DISCUSSION

Prof. P. DELAHAY (Baton Rouge):

(1) What is the maximum value of k_0 you could measure by radio-frequency polarography?

(2) Is the impedance of the electrode not entirely determined by the double layer capacity at such high frequencies?

DR. BARKER:

(1) Values of k_0 greater than 20 cm sec^{-1} can be determined in the case of aqueous solutions. With molten salts at high temperatures we expect to be able to use higher frequencies and then it may be possible to determine values of k_0 greater than 100 cm sec^{-1}.

(2) One of the main aims in R.F. polarography is to arrange that the interfacial impedance is controlled entirely by the double-layer capacity so that wave height varies linearly with concentration.

Dr. H. L. KIES (Delft):

(1) Is the basic principle of the square wave polarograph the same as that of the method of ISHIBASHI AND FUJINAGA?

(2) Is it to be expected that the basic current can be reduced by application of two capillaries?

DR. BARKER:

(1) I believe that the apparatus described by ISHIBASHI AND FUJINAGA is an elementary type of square wave polarograph.

(2) The capillary response can sometimes be reduced by the use of synchronised capillaries. However, due to changes with time in the water-repelling properties of the internal walls of the capillaries it is difficult to maintain good compensation over long periods of time. Twin capillaries can be more usefully employed in conjunction with the R.F. polarograph to eliminate waves produced by impurities in the base electrolyte.

Prof. B. BREYER (Sydney):

(1) A.C. polarographic waves are not just simple derivative curves of D.C. steps as is shown by results obtained in A.C. polarography of organic compounds and in tensammetry.

(2) For practical analytical purposes it is convenient to substitute irreversible electrode processes by reversible ones. Thus, *e.g.*, ferric ion is best analysed in oxalate solution, manganous ion in KCN solution, etc.

(3) It is often overlooked that the rise of current on the positive side of the electrocappilary zero point might be due to the discharge of halogen ions from the supporting electrolyte.

(4) Has Dr. BARKER tried siliconized capillaries?

(5) In measuring the reaction velocities by the use of low frequency A.C. polarography, has Dr. BARKER observed that the results obtained depend on the series resistance of the cell circuit?

Dr. BARKER:

(1) I agree with Prof. BREYER that A.C. polarographic waves are not just simple plots of the slope of the conventional polarographic step. The equations given in the text of the paper define the shapes of all reduction waves observed on a square wave polarogram.

(2) As regards the possibility of increasing sensitivity by making an irreversible reduction proceed more reversibly, my colleagues Mr. MILNER and Dr. FERRETT have used alkaline cyanide solution to obtain higher sensitivity in the determination of nickel and manganese.

(3) The marked rise in capillary response which is observed in square wave polarography on the positive side of the electro-capillary maximum is partly caused by specific adsorption of anions at such potentials. Continuous discharge of halogen ions does not usually occur within the range of potential which is studied.

(4) Siliconised capillaries have been used occasionally and polarogram B (Fig. 3) was obtained with such a capillary.

(5) In square wave polarography the internal resistance of the cell has only a small effect on wave height provided that it does not exceed 100 ohms.

Prof. W. KEMULA (Varsovie):

Does oxygen interfere in R.F. polarography?

Dr. BARKER:

Oxygen does not interfere to a greater extent than in normal square wave polarography. However, because of the increase in sensitivity at negative potentials, the second oxygen wave is much larger on a R.F. polarogram than on a square wave polarogram as is shown by Fig. 7.

OSZILLOPOLAROGRAPHISCHE MIKROANALYSE

von

ROBERT KALVODA

Polarographisches Institut der Tschechoslowakischen Akademie der Wissenschaften, Prag (Tschechoslowakei)

In der von HEYROVSKÝ eingeführten oszillographischen Wechselstrompolarographie ist die Kurve der Funktion $\frac{dE}{dt} = f(E)$ für die analytische Chemie von grösster Bedeutung. An dieser Kurve bezeichnet die Lage des Einschnittes an der Potentialachse die Qualität des Depolarisators, seine Fläche ist eine Funktion der Konzentration und kann in der nachfolgend beschriebenen Weise zu quantitativen Bestimmungen ausgenützt werden.

QUANTITATIVE BESTIMMUNG VON DEPOLARISATOREN

Bei der sogenannten Komparationstitration[1,2] werden am Leuchtschirm des Oszillographen zwei Kurven erhalten; die eine für die untersuchte Lösung, die andere für eine Grundlösung, die mit einer Masslösung des zu bestimmenden Depolarisators so lange titriert wird, bis beide Kurven identisch werden (Fig. 1). Bei der zweiten Methode wird die Entfernung der Spitze des Einschnittes von der Potentialachse mit Hilfe einer Einrichtung[3] gemessen, durch die am Leuchtschirm einerseits die Abbildung der $\frac{dE}{dt} = f(E)$-Kurve, anderseits eine durch ein kalibriertes Potentiometer in senkrechter Richtung verschiebbare waagrechte Achse projiziert wird (Fig. 2). Diese Einrichtung ermöglicht eine schnelle Bestimmung von Depolarisatoren mit Hilfe einer Eichkurve. Bei jeder, einem Punkt auf der Eichkurve entsprechenden Depolarisatorkonzentration stellt man mit dem kalibrierten Verschieber die projizierte Achse derart ein, dass sie die Spitze des Einschnittes auf der oszillographischen Kurve im Augenblick dicht vor dem Abreissen des Tropfens gerade berührt. Der entsprechende Wert, der die Tiefe des Einschnittes angibt (entspricht der zur Verschiebung der Achse zur Spitze des Einschnittes benötigten Spannung), wird am Verschieber abgelesen und in Abhängigkeit von der Konzentration aufgetragen. Die Eichkurve nähert sich in einem gewissen Konzentrationsbereich ($3 \cdot 10^{-4}$ bis $8 \cdot 10^{-4} M$) einem linearen Verlauf. Bei Konzentrationen oberhalb von $1.5 \cdot 10^{-3} M$ wächst der Einschnitt nahezu nicht mehr an und die Kurve strebt einem Grenzwert zu. Die Konstruktion der Eichkurve wird durch Ausmessung einer grösseren Anzahl von Standardkonzentrationen durchgeführt. Sowohl bei der Messung der Konzentrationsabhängigkeit als auch bei der Bestimmung einer Probe von unbekannter Konzentration muss der polarisierende Strom und die Gleichstromkomponente konstant gehalten werden. Eichkurven, die bei verschiedenen Wer-

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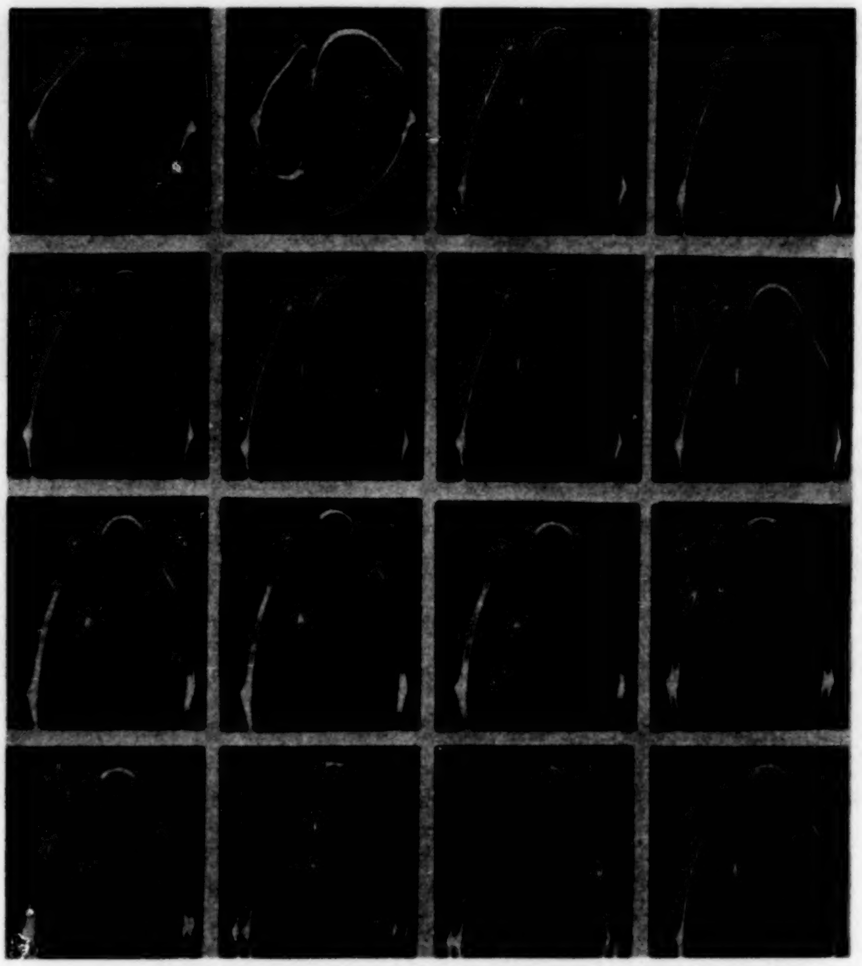

Fig. 1. Auschnitt aus einer komparativen Titration. In das erste Gefäss wurde zu 10.00 ml 1 *M* KOH Lösung 1.50 ml $2.0 \cdot 10^{-3} M$ Bleilösung zugegeben. (Am ersten Oszillogramm die Kurve mit dem Einschnitt.) Das zweite Gefäss enthielt 1. 0; 2. 0.90; 3. wie 2. aber höhere Verstärkung; 4. 1.00; 5. 1.10; 6. 1.20; 7. 1.30; 8. 1.35; 9. wie 8. aber die Kurven gegenseitig verschoben; 10. 1.40; 11. 1.45; 12. 1.50; 13. 1.55; 14. 1.65; 15. 1.75; 16. 1.85 ml $2.0 \cdot 10^{-3} M$ Bleilösung.

ten des polarisierenden Stromes und der Gleichstromkomponente ausgefertigt wurden, unterscheiden sich einigermassen voneinander, besonders in den Grenzen des Bereichs des steileren Anstieges bei niedrigeren Konzentrationen und im Bereich, bei welchem die Kurve dem Grenzwert zustrebt.

Diese Methode ist besonders bei Kontroll-Serienanalysen von Vorteil, wo die Lage der Achse in bezug auf die Kurve so eingestellt wird, dass die Einschnitte der Proben mit richtiger Konzentration die Achse berühren. Proben mit einem grösseren Gehalt an dem zu bestimmenden Stoff unterscheiden sich durch einen tieferen Einschnitt und umgekehrt. In ähnlicher Weise kann dieses Verfahren bei der Kontrolle der maximalen Verunreinigungen verschiedener Produkte verwendet werden. Die Lage der Achse wird so eingestellt, dass die Achse bei dem erlaubten Konzentrationsmaximum vom Einschnitt berührt werde. Proben mit grösseren Konzentrationen müssen für diese Bestimmung verdünnt werden, so dass sich die Endkonzentrationen des zu bestimmenden Stoffes im Konzentrationsbereich von 10^{-4} bis $10^{-3} M$ bewegen.

Die Fehler der Bestimmung bewegten sich im Bereich von 1 bis 10%; in der Regel überschritten sie nicht 3%.

DAS POLAROSKOP

Für praktische Zwecke wurde in letzter Zeit ein spezielles Röhren-Polaroskop* (Fig.

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* liefert KOVO A.G., Prag VII.

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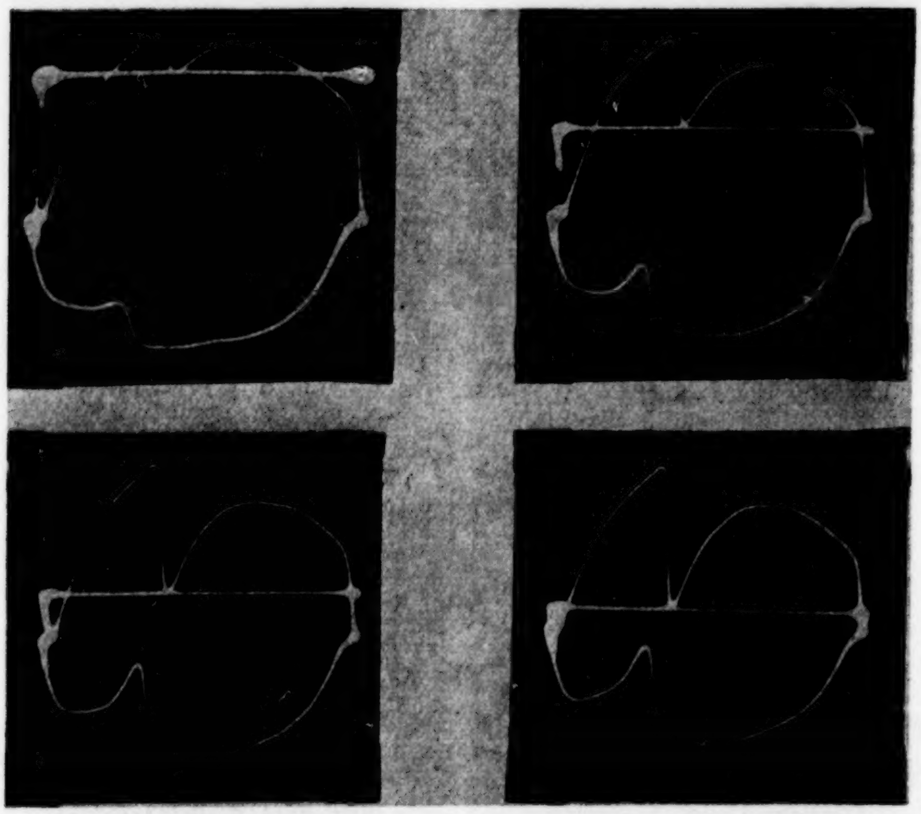

Fig. 2. Oszillopolarographische Kurven mit der waagerechten Achse. 1 M NaOH Lösung mit 1. 3.3; 2. 6.5; 3. 12.7; 4. $15.7 \cdot 10^{-4} M$ Bleilösung.

3) konstruiert, in welchem alle nötigen Geräte gemeinsam in einem Gehäuse untergebracht sind. Dieses Gerät ermöglicht ebenfalls die Durchführung beider oben beschriebenen quantitativen Messungen. Es ist auch ein Tropfenabreisser eingebaut, der zur Synchronisierung der Tropfzeit beider Kapillaren bei der Komparationstitration dient. Auch bei der Einschnittiefemessung ist es vorteilhaft, mit dem Tropfenabreisser zu arbeiten, da das exakte Einhalten der Tropfzeit der Elektrode das Erhalten von genauen und reproduzierbaren Ergebnissen bedingt. Damit die Elektrode nicht durch grosse Stromdichten, hauptsächlich im Augenblick dicht nach dem Abreissen des Tropfens belastet werde, wird die Elektrode erst in einem gewissen Augenblick nach dem Tropfenabreissen, wenn die Oberfläche schon genügend gross ist, polarisiert. Damit auch in Lösungen von geringerer Leitfähigkeit gearbeitet werden könne, ist im Gerät ein Kompensator für den Spannungsabfall in der Lösung eingebaut[4].

Dieses Polaroskop ermöglicht auch, die im weiteren ausführlich beschriebene mikroanalytische Bestimmung durchzuführen.

MIKROANALYTISCHE BESTIMMUNGEN

Die oszillographische Polarographie mit Wechselstrom ermöglicht die Bestimmung von Depolarisatoren im Konzentrationsbereich von 10^{-3} bis $5 \cdot 10^{-5} M$. Zur Bestimmung einiger Metalle im Konzentrationsbereich von 10^{-5} bis $10^{-9} M$ dient eine mikroanalytische Methode, die auf der vorherigen Abscheidung des zu bestimmenden Iones an einer stationären Quecksilberelektrode mit nachfolgender oszillopolarographischer Analyse der so entstandenen Amalgame beruht.

Die im Quecksilber kathodisch abgeschiedenen Metalle lösen sich im anodischen Verlauf wieder auf. Dieser Vorgang äussert sich durch typische Einschnitte an der $\frac{dE}{dt} = f(E)$-Kurve, deren Tiefe sich langsam mit fortschreitender Oxydation der Amalgame

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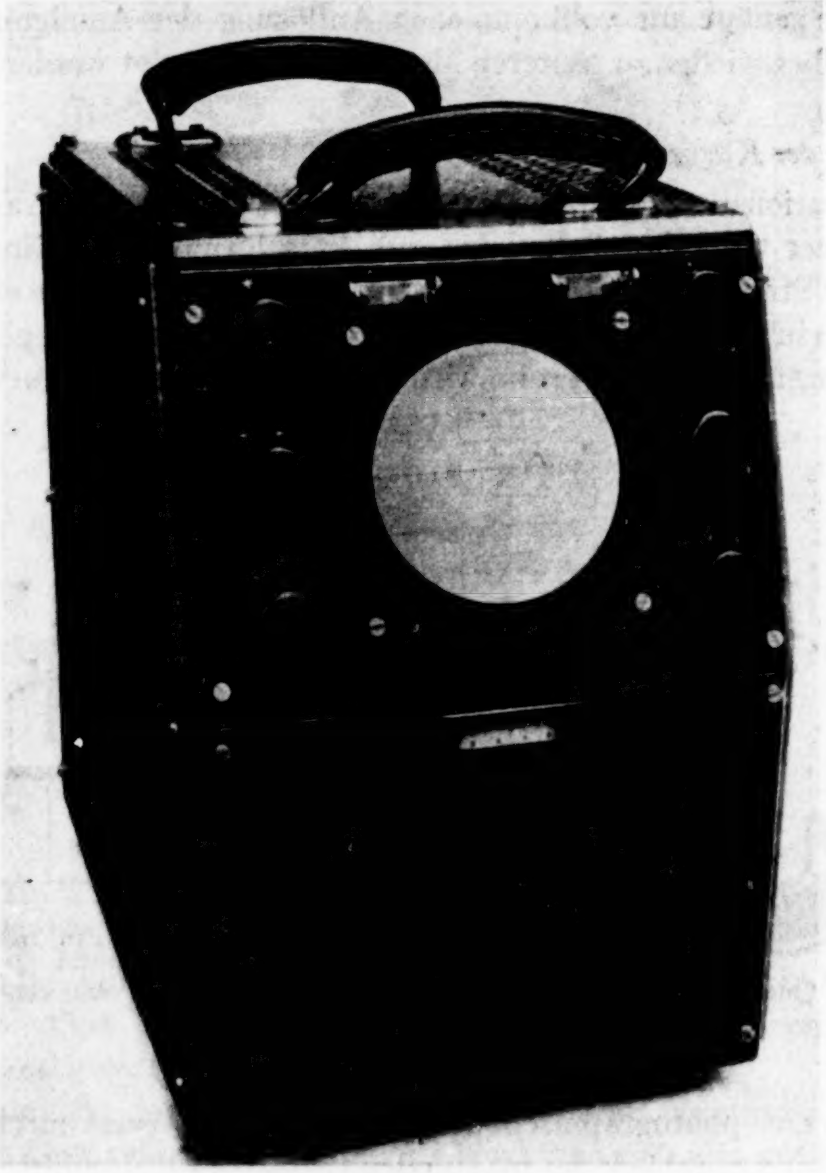

Fig. 3. Polaroskop P 576.

vermindert. So können Cu^{+2}-, Sn^{+2}-, Bi^{+3}-, Cd^{+2}-, In^{+3}-, Pb^{+2}-, Tl^{+}-, Zn^{+2}-, Ba^{+2}-, Sr^{+2}-, Na^{+}-, K^{+}-Ionen bestimmt werden.

Apparatur

Bei der Mikroanalyse wird eine stationäre Quecksilberelektrode verwendet (Fig. 4). Ein kleiner Behälter von etwa 5 mm Durchmesser enthält einen Quecksilbertropfen (*ca.* 0.03 ml), der die eigentliche Elektrode bildet. Dieser Behälter ist durch einen Platindraht mit dem Polaroskop verbunden. Damit die Lösung nicht unter den Tropfen eindringen könne, ist die Glasfläche silikoniert. Das Schema der Einrichtung ist in der Fig. 5 veranschaulicht. Die Kathode E wird durch Gleichstrom polarisiert, dessen Grösse durch den Widerstand R reguliert ist. Nach einer bestimmten Zeit, die zur elektrolytischen Abscheidung notwendig ist, wird die Elektrode durch den Schalter K mit dem Polaroskop verbunden. Als Anode dient hier eine Platinelektrode, deren Fläche etwa 2 cm² beträgt. Damit nicht nach jedem Experiment das Quecksilber in der Elektrode erneut werden müsse, bleibt die Elektrode nach der oszillopolarographischen Analyse mit dem Polaroskop weiter auf die Dauer von 2 bis 10 min verbunden.

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Diese Zeitdauer genügt zur vollkommenen Auflösung der Amalgame, so dass das gleiche Quecksilber wieder zu weiteren Messungen verwendet werden kann.

Die Auswertung der Kurven

Die Konzentrationsbestimmung wird mittels einer Eichkurve derart durchgeführt, dass die Zeitdauer vom Umschalten bis zum Verschwinden des Einschnittes an der Kurve mit einer Stoppuhr gemessen wird. Die so ermittelten Werte einiger Standardlösungen werden in eine Eichkurve gegen die Konzentration des Depolarisators eingetragen; die Konzentration der Probe wird dann von dieser Eichkurve abgelesen.

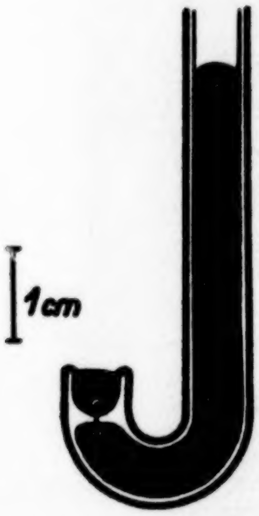

Fig. 4. Stationäre Quecksilberelektrode.

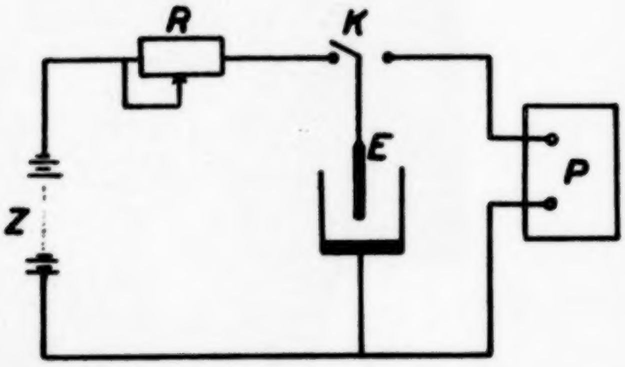

Fig. 5. Schema der Einrichtung zur Mikroanalyse: *Z*, 300 V; *R*, Widerstand, 50 kΩ; *E*, Kathode; *K*, Umschalter; *P*, Polaroskop.

Es kann auch eine photographische Registration in der Weise durchgeführt werden, dass die Kurve im Augenblick der maximalen Grösse des Einschnittes photographiert wird, d.h., dass das Umschalten von der Elektrolyse an das Polaroskop mit dem Verschluss der Kamera bei einer Belichtungszeit von 1/25 sec synchronisiert wird. Von der Figur wird dann die Grösse des Einschittes abgemessen und eine Eichkurve konstruiert (Fig. 6, 7).

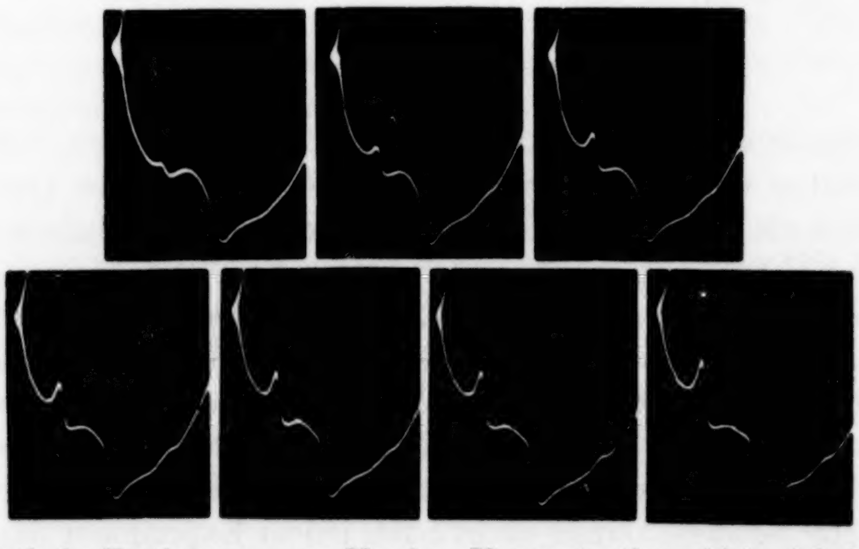

Fig. 6. Mikroanalytische Bestimmung von Kupfer. Konzentrationsabhängigkeit: Konzentration von Cu^{+2} (erste Reihe) 1. 0.5; 2. 1.0; 3. 1.5; (zweite Reihe) 4. 2.0; 5. 2.5; 6. 3.0; 7. $4.0 \cdot 10^{-6} M$ in 25 ml $1.5 \cdot 10^{-2} M$ H_2SO_4; 5 min lange elektrolysiert.

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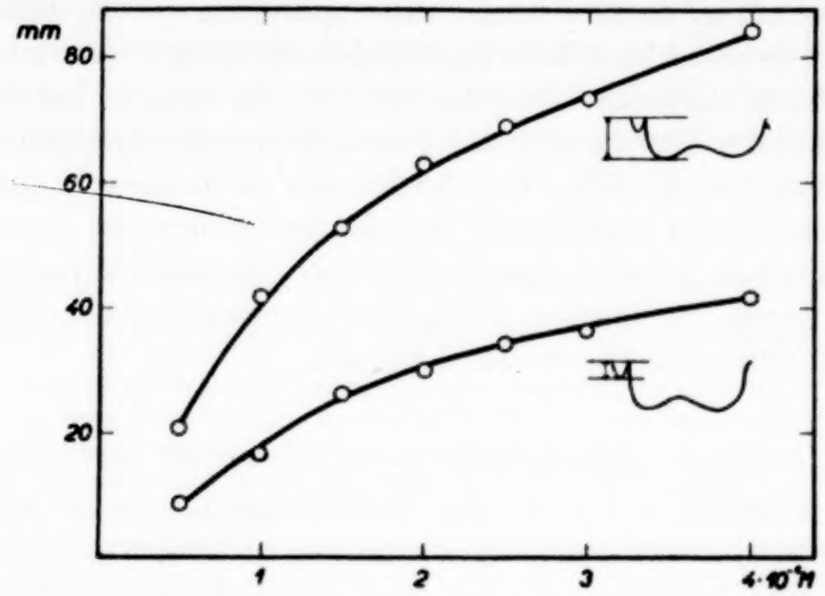

Fig. 7. Die Abhängigkeit der Grösse des anodischen Einschnittes von der Kupfer-Konzentration in $1.5 \cdot 10^{-2} M$ H_2SO_4.(Nach Fig. 6.)

Bedingungen der Elektrolyse

Bei der Anwendung von 10 ml einer $10^{-7} M$ Lösung ist schon nach 5 min dauernder Elektrolyse bei der Stromstärke von 25 mA ein gut entwickelter Einschnitt sichtbar. Bei Konzentrationen im Bereich von rund $10^{-8} M$ ist es notwendig, ein Volumen von 100 bis 200 ml 20 bis 60 min lang zu elektrolysieren. Bei noch kleineren Konzentrationen muss bei gleichzeitiger Erhöhung des Lösungsvolumens die Elektrolysendauer auf einige Stunden verlängert werden.

Als Grundlösung ist die Lösung einer Verbindung zu verwenden, dessen Kation sich nicht in das Quecksilber abscheidet. Es bewähren sich also am besten Lösungen von Säuren. Eine optimale Grundlösung bildet 0.015 bis $0.030 M$ Schwefelsäure, die vorher elektrolytisch gereinigt wurde.

Damit eine merkliche Abscheidung des in so niedrigen Konzentrationen vorliegenden Metalles bei der Anwendung von $0.015 M$ H_2SO_4 als Grundlösung stattfinde, ist es notwendig, eine so grosse Intensität des Gleichstromes zu benützen, dass sich die Elektrode wenigstens auf ein Potential von —1.3 V (gegen G.K.E.) polarisiere. Bei diesen Potentialen setzt bereits die Wasserstoffabscheidung ein, wodurch eine Strömung der Lösung und ein Wirbeln hervorgerufen wird. Wird die Elektrode auf negativere Potentiale polarisiert, so steigert sich das Wirbeln und die Einschnitte vergrössern sich bei gleicher Elektrolysendauer. Daraus ist ersichtlich, dass eine schnelle Metallabscheidung aus den Lösungen nur bei intensiver Konvektion in der Umgebung der Elektrode stattfinden kann.

Zu qualitativen Untersuchungen kann auch eine mit Quecksilber bedeckte Platinelektrode dienen, die durch elektrolytische Abscheidung eines Quecksilbertropfens vorbereitet wird. Die Einschnitte auf der Kurve verschwinden aber in diesem Falle schneller als bei Anwendung der vorher beschriebenen Elektrode. Es konnten so Einschnitte bereits nach 5 min langer Elektrolyse von 3 ml 10^{-8} bis $10^{-9} M$ Lösung von Cu^{+2}-, Cd^{+2}- und Zn^{+2}-Ionen beobachtet werden. Zu Bestimmungen von Depolarisatoren neben einem Überschuss an unedleren, ebenfalls Amalgame bildenden Depolarisatoren wurde eine mit Quecksilber bedeckte Vibrationselektrode verwendet. Die Elek-

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trolyse wurde in diesem Fall durch Anlegen einer Spannung durchgeführt, bei der nur die Abscheidung des gewünschten Ions stattfindet. Zu diesen Versuchen kann auch die vorher beschriebene stationäre Quecksilberelektrode dienen, bei der ein Rührer die nötige Konvektion der Lösung und des Quecksilbers gewährleistet.

Die Einschnitte von Na, K, NH_4, Ba und Sr wurden in einer Lösung von 0.05M Tetramethylammoniumjodid beobachtet. Bei der Elektrolyse ist es notwendig, mit kleineren Stromstärken zu arbeiten, damit die Elektrode nicht auf sehr negative Potentiale polarisiert werde, bei denen es infolge der Verminderung der Oberflächenspannung zu einer Zerstreuung des Quecksilbers kommt.

Bestimmungen bei Überschuss von anderen Depolarisatoren, die keine Amalgame bilden

Eine direkte Bestimmung ist nur in dem Falle möglich, wo die Einschnitte des untersuchten und des überschüssigen Depolarisators nicht koinzidieren. Bei Koinzidenz, oder bei grossem Überschuss, bei dem auch eine Deformation der Kurve auftreten könnte, wird das verfolgte Kation in das Quecksilber abgeschieden, und die oszillopolarographische Messung wird nach Auswechseln der Lösung gegen die geeignete Grundlösung durchgeführt. Während des Abspülens der Elektrode mit 0.001M H_2SO_4 sowie des Auswechselns der Grundlösung wird die Kathode durch Gleichstrom weiter polarisiert. So wurde eine Analyse von Kadmium oder Blei im Verhältnis $1:10^5$ bis $1:10^6$ neben Eisen oder Uran durchgeführt[5]. Die Methode, bei der die analysierte Lösung vor der oszillopolarographischen Messung gegen eine geeignete Grundlösung ausgewechselt wird, ist vorteilhaft bei der Analyse von Materialen, die organische Bestandteile enthalten.

Reinheitskontrolle von Chemikalien

Von der zu prüfenden Substanz wird eine Lösung von bestimmter Konzentration bereitet, die durch Zugabe von Schwefelsäure angesäuert wird (Konzentration der Säure etwa 0.01 bis 0.05M). Bei der Identifikation von Spuren von Depolarisatoren (etwa 0.001%) genügt eine 5 min lange Elektrolyse von 5 ml Lösung. So kann z.B. die Anwesenheit von Cu, Pb und Zn in Kaliumchlorid, Kaliumsulfat, Natriumacetat usw. nachgewiesen werden.

BEWERTUNG

Die Komparationstitration bzw. die Messung der Einschnittiefe kann in allen Fällen benützt werden, wo in Anwesenheit von Depolarisatoren ein Einschnitt auf der oszillopolarographischen Kurve entsteht, dessen Grösse von der Konzentration abhängig ist. Die Bestimmungen lassen sich im Konzentrationsbereich von etwa $8\cdot10^{-5}$ bis $8\cdot10^{-4}M$ gut durchführen. Konzentrierte Lösungen sind zu verdünnen. Dieser erwähnte Bereich kann aus der Form der Kurve gut erkannt werden; die Grenzkonzentration ist erreicht, wenn die Spitze des Einschnittes sich der die beiden Endpunkte verbindenden Achse annähert.

Die oszillographische Polarographie kann auch zur Analyse einiger Depolarisatoren in niedrigen Konzentrationen von 10^{-5} bis $10^{-9}M$ dienen. Die Fehler bei der quantitativen Auswertung, bei der die zum Verschwinden des Einschnittes benötigte Zeit gemessen wird, erreichten nur vereinzelt 30 bis 40%. Durchschnittlich überschreiten sie jedoch nicht 15 bis 25%. Die geringere Genauigkeit wird hier durch die Einfachheit

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und Schnelligkeit der Bestimmung aufgewogen. Genauer, jedoch langwieriger ist das Verfahren, das die photographierte Kurve auswertet, bei der sich der mittlere Bestimmungsfehler zwischen 3 bis 5% bewegt. Eine wesentliche Verkürzung könnte durch direkte photographische Registrierung auf empfindliches Papier erreicht werden.

ZUSAMMENFASSUNG

In der oszillographischen Polarographie mit Wechselstrom werden für Zwecke der quantitativen Analyse die Kurven $\frac{\mathrm{d}E}{\mathrm{d}t} = f(E)$ vervolgt. Es wird eine Komparationstitration vorgeschlagen, bei der auf dem Leuchtschirm zwei Kurven beobachtet werden: die eine für die untersuchte Lösung, die andere für eine Vergleichslösung, die mit einer Masslösung des zu bestimmenden Depolarisators so lange titriert wird, bis beide Kurven identisch werden.

Bei der zweiten Methode wird die Entfernung der Spitze des Einschnittes von der Potentialachse mit einer speziellen Einrichtung gemessen.

Zur Bestimmung einiger Metalle im Konzentrationsbereich von 10^{-5} bis $10^{-9}M$ dient eine mikroanalytische Methode, die auf der vorangehenden Abscheidung des zu bestimmenden Ions an einer stationären Quecksilberelektrode mit nachfolgender oszillopolarographischer Analyse der so entstandenen Amalgame beruht.

SUMMARY

In oscillographic polarography with alternating current, curves representing the functions $\frac{\mathrm{d}E}{\mathrm{d}t} = f(E)$, were employed for the purpose of quantitative analysis. A comparative titration was proposed, in which two curves were observed on the luminescent screen; one for the solution being analysed, the other for a comparison solution, which was titrated with a standard solution of the depolarizer being determined, until the two curves were identical.

In the second method, the distance of the peak of the cut-in from the potential axis was measured with special equipment.

For the determination of several metals in the concentration range from 10^{-5} to $10^{-9}M$ a micro-analytical method was used, which is based on the previous separation of the ions to be determined at a stationary mercury electrode with subsequent oscillo-polarographic analysis of the amalgam formed.

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POLAROGRAPHISCHE UNTERSUCHUNGEN CYTOSTATISCHER CHINONDERIVATE

von

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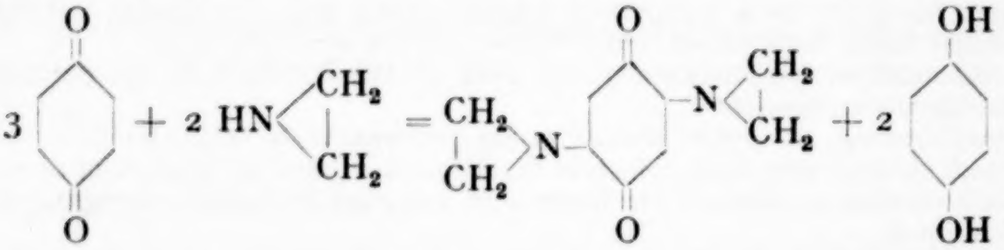
EINLEITUNG

Unter den Äthylenimino[1]- und N-Lost-Derivaten[2] des *p*-Benzochinons wurden Cytostatika beträchtlicher Wirksamkeit aufgefunden. Für diese Hemmeffekte dürften neben den cytostatisch aktiven Substituenten[3] auch die veränderten Redox-potentiale bedeutsam sein. Zur Beantwortung dieser Frage kann eine polarographische Untersuchung wesentlich beitragen und weiterhin über den Lösungszustand dieser Depolarisatoren aussagen[4].

Obige Verbindungen entstehen über Redoxreaktionen nach dem Schema[5]:



und bilden überwiegend schwerlösliche, zumeist tieffarbige Kristalle. Wie sich im Verlauf unserer polarographischen Untersuchungen zeigte, ergaben sich sowohl hinsichtlich Bildungsweise als auch Stufenform deutliche Parallelen zu der Arbeit von WIESNER[6] über Reaktionsprodukte zwischen *p*-Benzochinon und Aminosäuren.

EXPERIMENTELLE ERGEBNISSE

Die polarographischen und polaroskopischen Aufnahmen erfolgten in der üblichen Weise, wie an anderer Stelle ausführlicher dargestellt wird, unter Verwendung von Aceton-Wasser-, Äthanol-Wasser-, Dioxan-Wasser-Gemischen mit Zusatz von LiCl, Phosphat- oder Britton-Robinson-Puffer als Leitlösungen.

Unter Aufnahme von zwei Elektronen in die Chinongruppe bilden sich reversibel Hydrochinone, wobei je nach Lösungsmedium eine oder zwei Stufen registriert werden, deren konzentrationsproportionale Gesamthöhe diffusionsbegrenzt ist (Fig. 1a, b).

Die Halbstufenpotentiale verändern sich im Mittel um 60 mV/pH und liegen bis zu —1.1 V negativer als das des *p*-Benzochinon (vgl. Fig. 2 und Tabelle I).

Besonders häufig werden Doppelstufen bei den Chinonen VI, VII, VIII, IX, u. X gefunden (Fig. 1 c, d).

Eine nähere Untersuchung an Chinon VII in verschiedenen Leitlösungen spricht für ein Gleichgewicht zwischen zwei Chinonformen, die zum gleichen Hydrochinon reduziert werden (Fig. 1c). Im wäßrigen schwach sauren Phosphatpuffer (Fig. 1d) bildet

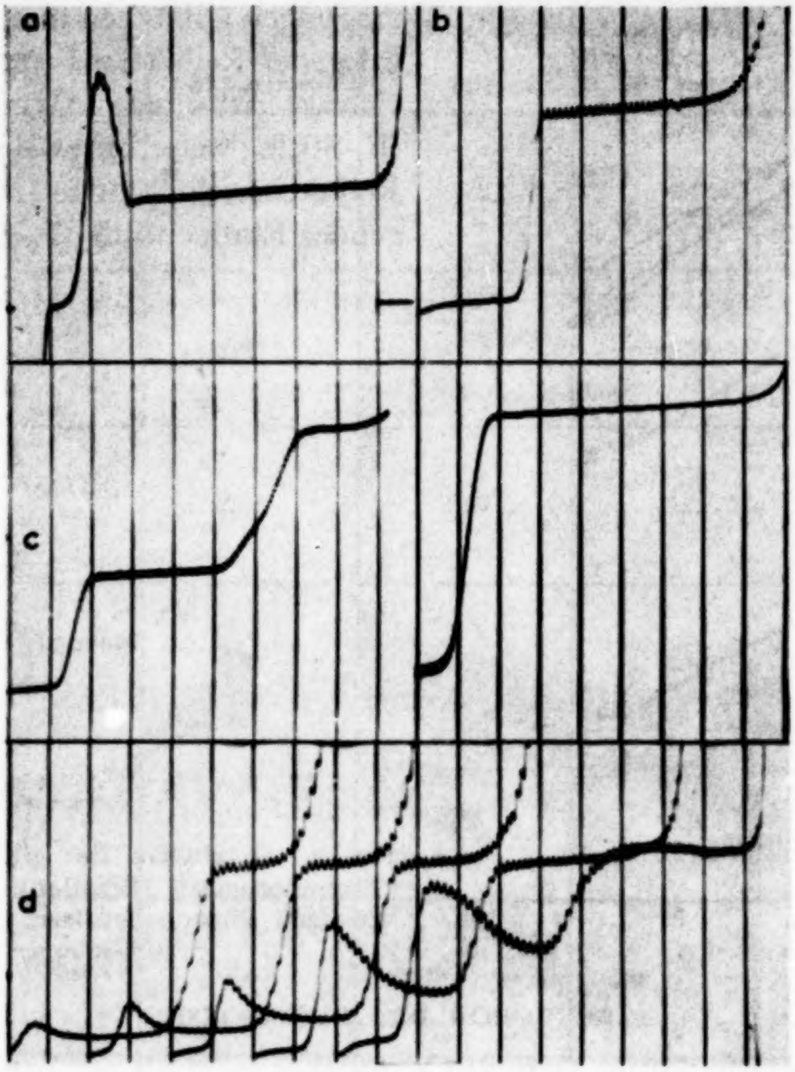


Fig. 1. Polarogramme von $5 \cdot 10^{-4} M$ Chinonen bei verschiedenen Empfindlichkeiten ($\Delta\pi = 0.2$ V).
(a) Chinon VII in $0.05 M$ H_2SO_4, 80% Aceton (Kohleanode) ab + 0.4 V
(b) Chinon III in Phosphatpuffer pH 7 (N.C.E.) ab 0 V
(c) Chinon VII in Phosphatpuffer pH 8 + Pd-Sol (Gummi arabicum). Links: Reduktionsstufen; rechts: Oxydationsstufe nach Begasung mit Wasserstoff.
(d) Chinon VII in Phosphatpuffern pH 4.9 – 5.9 – 7 – 8 – 9 (N.C.E.) ohne Dämpfer.

sich die leichter reduzierbare Form (F_1) und ihre Stufenhöhe wächst mit steigendem pH-Wert. Bemerkenswert sind das Maximum des F_1-Grenzstromes (Fig. 1d) und eine Adsorptionsstufe im Stufenanstieg von F_2, die in bestimmten Leitlösungen das Bild der Doppelstufe stark deformieren können. Dextran- oder Äthanolzusatz können diese Störungen beseitigen (Fig. 3).

Beide Teilstufen sind linear von der Höhe des Quecksilberniveaus abhängig. Temperatursteigerung vergrößert die Summe der Grenzströme um 1.4% Grad, wobei F_1 auf Kosten von F_2 von 16% (bei 25°C) auf 72% (bei 75°C) der Gesamtstufe anwächst (Fig. 3).

Die Geschwindigkeit der Reduktion mittels Pd-Sol hängt von den Halbstufenpotentialen nach Art einer modifizierten Dimroth-Gleichung[7] ab. Für Doppelstufen ist dabei das F_1-Potential maßgebend.

Die $\frac{d\pi}{dt} - \pi$ - Aufnahmen mit dem Polaroskop P-524 ergeben bei einstufigen Derivaten Bilder (Fig. 4a) mit gegenüberliegenden Einschnitten. Das Doppelstufenchinon VII verhält sich selbst an der strömenden Elektrode (Fig. 4d) komplizierter. Je nach Be-

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dingungen entstehen maximal: ein positiv gelegener Reduktions- und gegenüber ein charakteristischer Oxydationseinschnitt (F_1-Stufe); weiterhin zwei negative variable Reduktionseinschnitte mit gegenüberliegender Einbuchtung (F_2-Stufe).

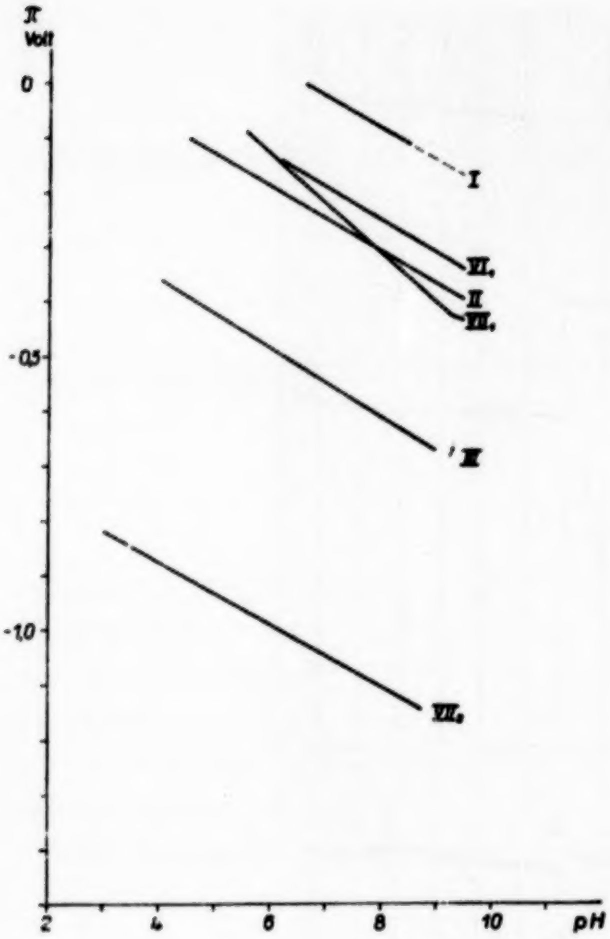
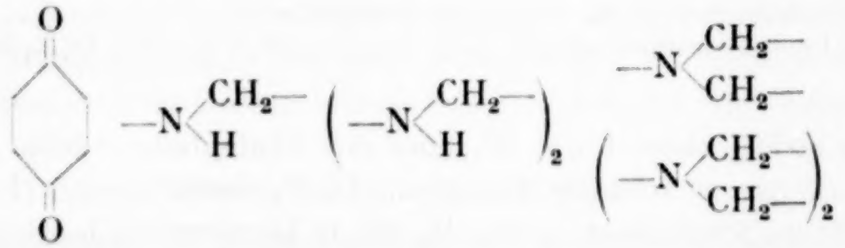


Fig. 2. Diagramm der pH-Abhängigkeit von Chinonderivaten (Bezifferung s. Tabelle I) in wäßrigen Phosphatpuffern.

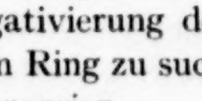
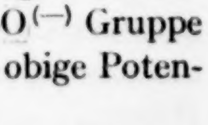
DISKUSSION DER ERGEBNISSE

Wenn man das bromhaltige Derivat IX, welches mehr als $2e^-$ aufnimmt, außer Betracht läßt, ergeben alle Depolarisatoren eine starke Negativierung gegenüber dem Halbstufenpotential des *p*-Benzochinons:



—0.025 —0.25 —0.55 —0.3 —1.1 Volt

in welches Schema sich auch die WIESNER'schen Messungen[6] sehr gut einfügen. Die Ursache der erschwerten Reduktion ist in einer Negativierung der $>C—O^{(-)}$ Gruppe durch Elektronenverschiebung vom Stickstoff zum Ring zu suchen und obige Potentialdifferenzen ergeben ein Maß für die Resonanzenergien.

Der auffallende Unterschied zwischen den  $—N\begin{smallmatrix}CH_2— \\ H\end{smallmatrix}$ und den  $—N\begin{smallmatrix}CH_2— \\ CH_2—\end{smallmatrix}$ Derivaten besteht in der Tendenz letzterer, zwei polarographisch meßbare Gleichgewichtsformen (F_1 und F_2) mit der bei Chinon VII beträchtlichen Potentialdifferenz von 0.8 V (≙ 37 kcal) zu bilden. Vorerst wollen wir diese Teilstufen den mesomeren Grenzstrukturen[6] zuordnen, deren jeweiliger Anteil vom Lösungsmedium und der Temperatur (Thermochromie) abhängt.

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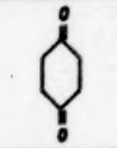
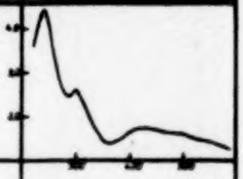
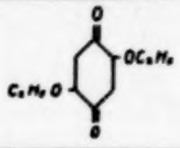
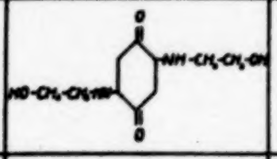
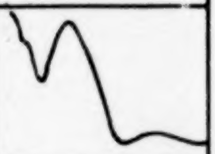
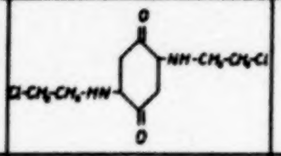
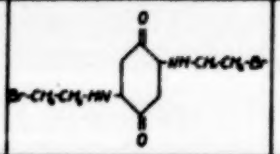
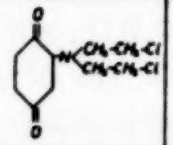
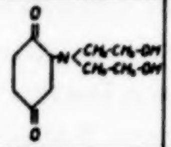
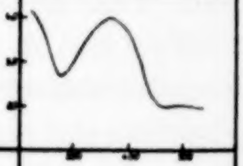
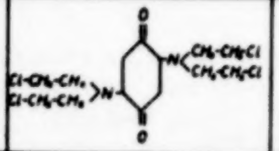
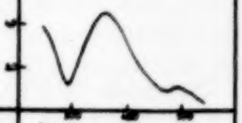
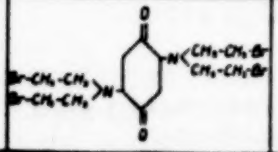
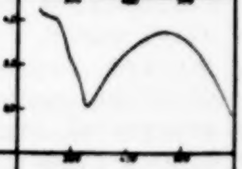
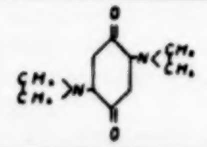
Nr.	Formel	0,05m H_2SO_4 80% Aceton		0,2m LiCl 80% Dioxan		0,2m NH_4OH/NH_4Cl 0,1m LiCl (pH 6,5) 80% Aceton		Spektrenauswahl
I		0,0		-0,28		-0,12		
II		-0,05		-0,53		-0,30		
III		-0,26		-0,87		-0,60		
IV		-0,30		-0,84		-0,54		
V		-0,33		-0,85		-0,54		
VI		-0,07		-0,52	—	-0,18	—	
VII		0,0		-0,53	-1,52	(-0,2)	-1,3	
VIII		-0,05		(-0,5)	—	-0,19	-0,35	
IX		+0,02	-0,055	-0,29	-0,460	-0,17	—	
X		-0,06	-0,25	-4+40	-1,20	-0,190	-0,38	

Tabelle 1. Struktur, Halbstufenpotentiale (gegen N.C.E.) und typische Absorptionsspektren (Lsgm. H_2O oder $CHCl_3$) von Chinonderivaten. Die HSP-Werte in der Spalte: 0.05*M* H_2SO_4, 80% Aceton sind relativ, da sie mit der Kohleelektrode ohne Zusatz von Maximadämpfer ermittelt wurden.

In den Spektren (Tabelle 1) unterscheiden sich die Chinonderivate deutlich von der Stammsubstanz, indem die langwelligste Ringbande durchschnittlich bis auf 360 mμ, bei Chinon IX, welches schon polarographisch eine Ausnahme darstellt, sogar bis auf 460 mμ verschoben wird. Für die Banden im Sichtbaren geht die Verschiebung nach

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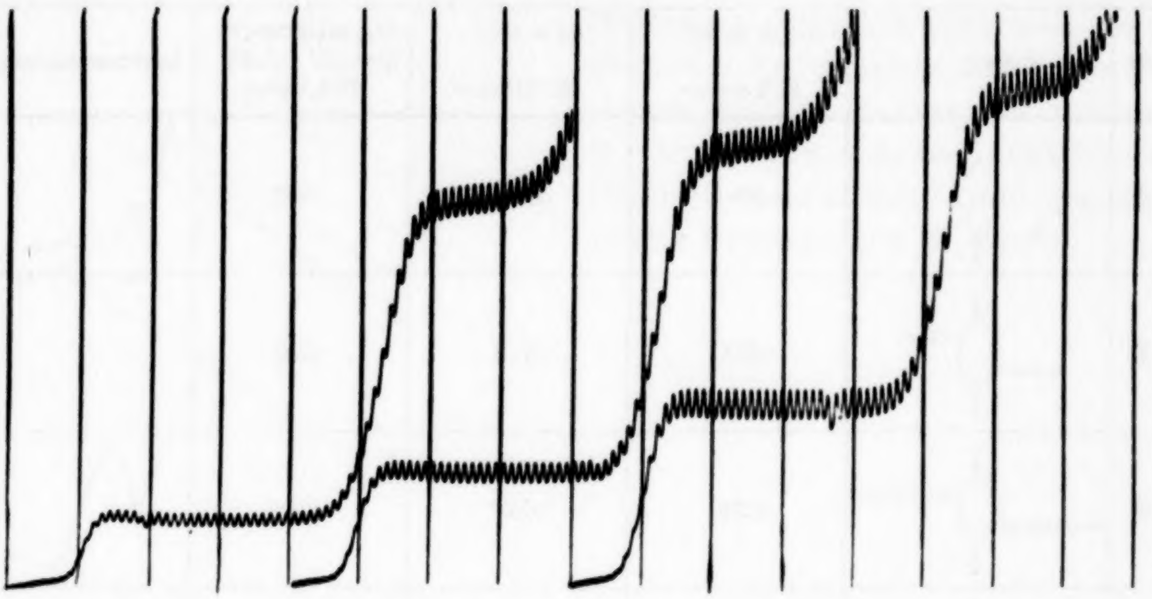

Fig. 3. Temperaturabhängigkeit der Stufenhöhen von Chinon VII bei 25°, 35.2°, 45.2°C (Phosphatpuffer 0.15M Na_2HPO_4 mit 10% Äthanol).

längeren Wellen im allgemeinen parallel mit einer erleichterten Elektronenaufnahme bzw. Erhöhung der chemischen Reduktionsgeschwindigkeit.

Es verdient Beachtung, daß die einleitend erwähnte starke therapeutische Wirksamkeit bisher nur bei solchen Derivaten gefunden wurde, deren Halbstufenpotentiale (in Phosphatpuffer mit pH 7) positiver als —0.5 V gegen die N.C.E. liegen. Hierzu zählen auch die doppelstufigen Depolarisatoren VI, VII, VIII, IX, X, von denen die Form F_1 stets relativ leicht reduziert wird. Unsere vorläufigen Ergebnisse führen zu dem Schluß, daß eine wichtige Voraussetzung für das Mitreagieren dieser Chinon-Cytostatika im Zellstoffwechsel in ihren den Cofermenten und biologischen Substraten[8] angepaßten Redoxpotentialen liegt. Zu entsprechenden Folgerungen kamen PAGE UND ROBINSON[9] mit bakteriostatischen Chinonderivaten, jedoch ist in jedem Falle die spezifische Substituentenwirkung[3] entscheidend beteiligt.

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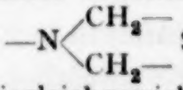
ZUSAMMENFASSUNG

Äthylenimin — und N-Lost-Derivate des *p*-Benzochinons werden unter verschiedenen Bedingungen polarographisch charakterisiert. Einige Depolarisatoren mit  $—N\begin{matrix}\diagup CH_2— \\ \diagdown CH_2—\end{matrix}$ Substituenten ergeben Doppelstufen, welche auf ein temperaturabhängiges Mesomeriegleichgewicht deuten.

Wenn die Halbstufenpotentiale positiver als —0.5 V gegen die N.C.E. (bei pH 7) liegen, erhöht

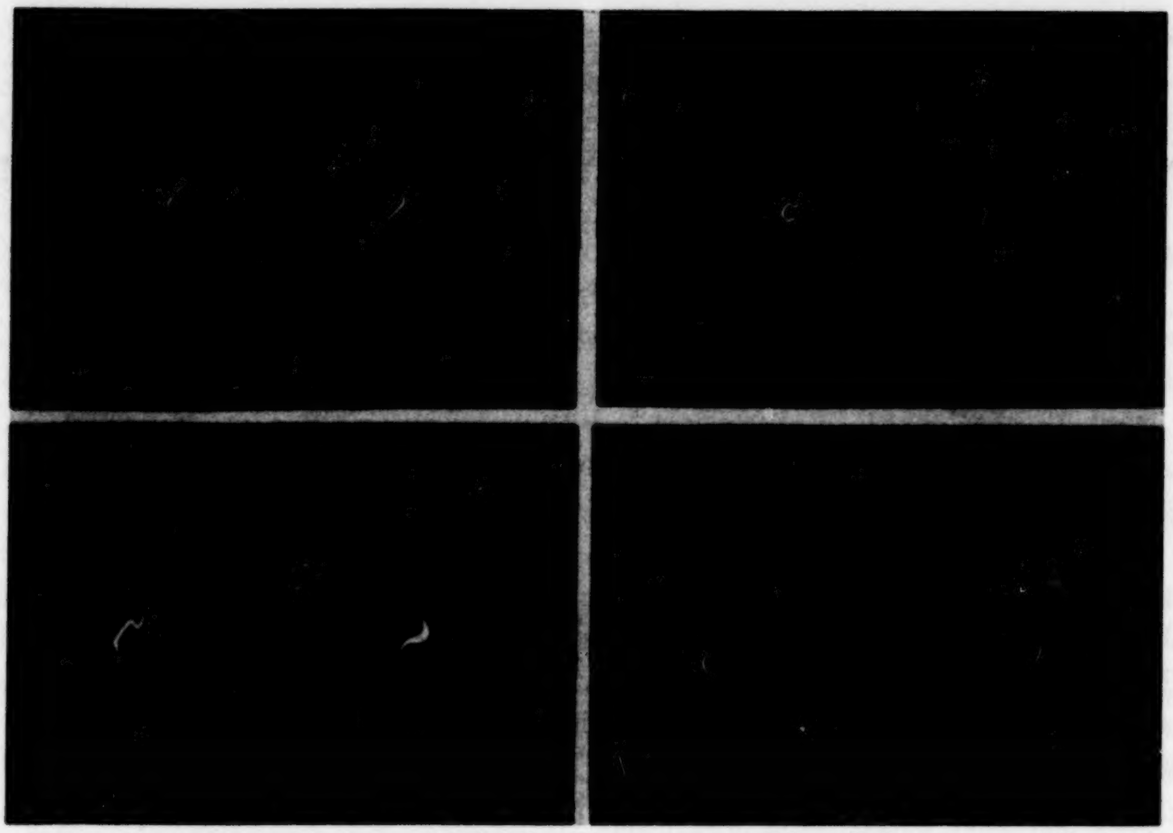
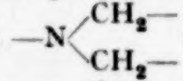


Fig. 4. Polaroskopische Aufnahmen (Objektiv Biotar, 17/10 Film, Bel. 1/25 sec, Wechselstrom: 0.2 mA bis 1.2 mA) von:
(a) Chinon III (Tropfelektrode, $5 \cdot 10^{-4} M$, pH 4.6); (b) Chinon VII (Tropfelektrode, $5 \cdot 10^{-4} M$, pH 4.6); (c) Chinon VII (Tropfelektrode, $5 \cdot 10^{-4} M$, pH 8.6); (d) Chinon VII (strömende Elektrode, $5 \cdot 10^{-4} M$, pH 8.6).

sich der cytostatische Effekt, was für weitere Synthesen in dieser Verbindungsklasse, sowie ihren Wirkungsmechanismus in der Zelle bedeutsam werden kann.

SUMMARY

Ethyleneimine- and N-mustard derivatives of *p*-benzoquinone were differentiated under various polarographic conditions. Several depolarizers with  $—N\langle{}^{CH_2—}_{CH_2—}$ substituents yield double steps, which indicate a mesomeric equilibrium dependent upon the temperature. When the half-wave potential, against the N.C.E. (pH 7), is more positive than —0.5 V, the cytostatic effect is increased. This fact may be significant for further syntheses in this group of compounds as well as for the mechanism of their action in the cell.

DISKUSSION

Prof. Dr. B. **Breyer** (Sydney):

(1) Das Redoxpotential spielt eine grosse Rolle bei der biologischen Wirkung von organischen Verbindungen, wie in früheren Arbeiten auf dem Gebiet der Phenylarsonsäurederivate (Breyer, 1938) und Acridinverbindungen (Breyer, Buchanan und Duewell, 1943) gezeigt wurde.

(2) Vielleicht wäre es möglich die schwerlöslichen Benzochinonderivate mittels der hochempfindlichen tensametrischen Methode zu untersuchen.

Dr. H. **Berg**:

(1) Eine Voraussetzung zur Afklärung des cytostatischen Reaktionsmechanismus bildet die umfassende Kenntnis der Substanzeigenschaften und deren mögliche Beziehungen zur Wirksamkeit. Dem Redoxpotential (bzw. Halbstufenpotential) ist dabei zweifellos besondere Aufmerksamkeit zu widmen, da es sowohl seitens der Substituenten (also auch der pharmakodynamisch aktiven) beeinflußt wird, als auch ein Maß für Reaktionsfähigkeit in Redoxprozessen sein kann.

(2) Den freundlichen Hinweis auf die Tensametrie können wir erst noch der vollständigen Aufklärung der z.T. komplizierten Stufenbilder mit den Mitteln der klassischen Polarographie verwirklichen.

Die in der Tabelle 1 angegebenen Halbstufenpotentiale gehören nicht nur zu Gleichgewichtsstufen, sondern auch zu dem katalytischen Wellen (bes. ausgeprägt bei X u. dem Präparat Bayer E 39) sowie Adsorptionsstufen. Auch bedarf die Ursache der besonders hohen Stufe von IX noch weiterer Klärung.

POLAROGRAPHIE UND OSZILLOGRAPHIE DES VITAMINS B$_1$ VOM ANALYTISCHEN STANDPUNKT

von

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Zum Unterschied von der Weltbibliographie, die in der oszillographischen Polarographie besonders eine Beschleunigung oder eine Steigerung der Genauigkeit der chemischen Analyse erblickt, nützt die Prager Schule Prof. HEYROVSKÝS den Röhren-Polarographen vor allem zur Vertiefung der Kenntnisse über die Erscheinungen der klassischen Polarographie aus. Es handelt sich insbesondere um das Studium des Mechanismus schneller Elektrodenprozesse, das Erfassen von Zwischenprodukten mit kurzer Lebensdauer, die Unterscheidung verschiedener Depolarisatoren, die Geschwindigkeit ihrer Abscheidung u.a. Die Oszillopolarographie ist nahezu ideal für die Verfolgung der Stabilität von Verbindungen, sofern es sich um elektroaktive Komponenten handelt, so dass sie in letzter Zeit auch bei der Erforschung der Vitamine in steigendem Masse Verwendung findet. Am Beispiel der Polarographie und Oszillographie des Thiamins möchte ich versuchen, diese so vielversprechenden Perspektiven anzudeuten.

Die in zahlreichen polarographischen Arbeiten beschriebenen katalytischen[1–17] und oberflächenaktiven[18] Wirkungen des Thiamins in gepufferten und ungepufferten Lösungen sowie in der Brdička-Solution[19] sind nur von beschränkter analytischer Verwendbarkeit. So ermöglicht die von WIESNER[19] vorgeschlagene katalytische Stufe (die sog. Praenatriumstufe) in Phosphatpuffer vom pH etwa 7 zwar die Bestimmung einiger μg Thiamin in 1 ml Lösung, doch ist sie wegen ihrer Unspezifität nur in den einfachsten Medien, wie z.B. der Pharmaceutika, verwendbar. Dasselbe gilt für die stark pH-abhängige Reduktionsstufe des Thiamins in alkalischerem Milieu[20,21], wo sich ebenfalls eine katalytische Komponente geltend machen kann. Unspezifisch ist gleichfalls die Bestimmung nach GÜNTHER[22] auf Grund der Hydrochlorid-Komponente des Thiamins, oder die indirekte Methode nach PLETICHA[23,24], die auf der Ausfällung des Thiamins durch BiJ$_4^-$-Ionen, dem Auflösen des isolierten Niederschlags in einer Kalium-Natrium-Tartrat-Lösung und der Registration der anodischen Jodidstufe beruht. Derselbe Autor schlug eine Bestimmung des Thiamins auf Grund seiner elektroaktiven Formen in alkalischem Milieu vor, wobei die Ausmessung der Höhe der anodischen Stufe durch Aufnahme der Ableitungskurven[25,36] genauer gemacht werden kann. Da es sich auf Grund einer eingehenderen polarographischen[15–17, 19–21, 25–37] und oszillographischen[17,38] Untersuchung unter gewissen Bedingungen um genügend stabile -SH und -SS-Formen des Thiamins handelt, ist diese Bestimmung mit Rücksicht auf die polarographische Aktivität der übrigen Vitamine[39,40] und auf die verhältnismässig geringere Anzahl der anodisch depolarisierenden Stoffe spezifischer.

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In Verbindung mit der Papierverteilungschromatographie wurde einerseits die katalytische Stufe des Thiamins für dessen Bestimmung im Pflanzenmaterial[41] und weiter die anodische Stufe der Thiolformen für die Bestimmung in Gegenwart von einen positiven Thiochrom-Test liefernden Stoffen[34–36] benützt. Am schwierigsten ist bei der Polarographie des Thiamins seine Bestimmung in natürlichem Material, wo, wie eine vorläufige Studie[37] gezeigt hat, die Polarographie mit der Adsorptionschromatographie oder mit der Anwendung von Ionenaustauschern kombiniert werden muss.

Im nachfolgenden experimentellen Teil wird oszillographisch-polarographisch einerseits ein neues, grün lumineszierendes Abbauprodukt des Thiamins vom Standpunkt der pharmazeutischen Analyse untersucht und weiter die Elektroaktivität der Cocarboxylase und die Stabilität des Thiamins geprüft, als Beitrag zum Problem der polarographischen Bestimmung des Gesamtvitamins B_1 in natürlichem Material auf nichtenzymatischem Wege.

EXPERIMENTELLER TEIL

Die polarographischen Kurven wurden wie gewöhnlich mit dem Polarographen Heyrovský-Nejedlý, Type VIII, registriert. Die Oszillogramme der Abhängigkeit $dV/dt = f_1(V)$ wurden mit dem Röhren-Polaroskop P-524 der Firma Křižík, n.p., Prag verfolgt. Die Kurven wurden mit der Kamera Contax D bei der Lichtstärke 2.0, der Belichtungsdauer von etwa 1-2 sec und der Empfindlichkeit des Negativmaterials 17/10° DIN photographiert.

GELBGRÜN LUMINESZIERENDES PRODUKT DES THIAMINS

Aus dem kurzen Umriss der bisherigen Polarographie des Thiamins ist ersichtlich, dass bisher kein Versuch unternommen wurde, die leichte Oxydierbarkeit dieses Stoffes analytisch auszunützen. Während das durch mässige Oxydation gebildete, blau lumineszierende instabile Thiochrom als polarographisch inaktiv befunden wurde[17,42], kann aus der oszillographischen Beobachtung auf die Elektroaktivität seiner Zersetzungsprodukte in alkalischem Milieu geschlossen werden[17]. Demgegenüber weist das zweite bekannte Produkt der Oxydation in alkalischem Medium, das Disulfid des Thiamins, keine Lumineszens auf, liefert jedoch eine vollkommen reversible, ausgeprägte kathodische Stufe, deren Höhe pH-unabhängig ist[20,31,33]. Erst in stark alkalischem Milieu geht diese kathodische Stufe in die typische anodische Welle der Thiolform entweder direkt des Disulfids oder des abgespaltenen Thiamins über. Die Ergebnisse von Versuchen über die indirekte Bestimmung des Thiamins in Heilmitteln nach Überführung in Disulfid durch Einwirkung von Jod und Entfernung des überschüssigen Jods durch Thiosulfat oder Sulfit sollen später veröffentlicht werden[43].

Vom analytischen Standpunkt bleibt die neu gewonnene gelbgrün lumineszierende Substanz eine offene Frage, die ich durch Behandlung des Thiamins mit 30%igem Perhydrol oder Natriumperoxyd in alkalischem Milieu erhalten habe. Nach vollständigem Auskochen des frei gewordenen Sauerstoffes aus dem leuchtend gelbgrün lumineszierenden wässrigen alkalischen Reaktionsgemisch wird bereits kein weiterer, im UV-Licht lumineszierender Stoff in Isobutanol ausgeschüttelt und der Jansensche Thiochromtest ist negativ, was auf einen quantitativen Abbau des Thiamins hinweist. Wird dem Gemisch weiter eine Spur von Thiamin zugesetzt, so ist nach Ausschütteln und Abtrennung beider Schichten im UV-Licht in der oberen Butanolschicht eine intensive, typisch blaue Thiochromlumineszenz sichtbar, während die untere wässrige alkalische Schicht gelbgrün lumineszierte. Das isolierte Produkt* ist gelb, amorph, hy-

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* Die Isolierung und weitere Untersuchung wird später veröffentlicht werden.

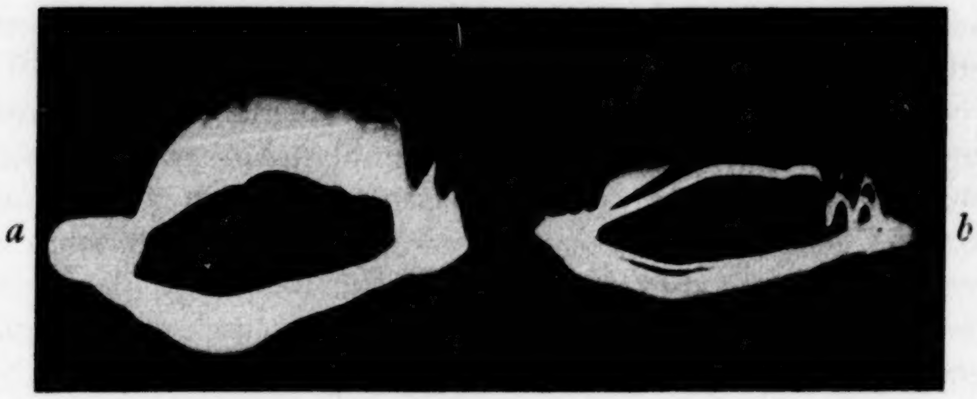

Fig. 1.

Kurve (a): Oszillogramm des Thiaminabbauproduktes in 10-mal konzentrierterer Acetat-Pufferlösung vom pH 4.4.

Kurve (b): Oszillogramm von 2-Methyl-4-amino-5-äthoxymethyl-pyrimidin bei gleichen Bedingungen wie unter (a). Quecksilbertropfelektrode, N_2-Atm., gegen ges. Kalomelelektrode.

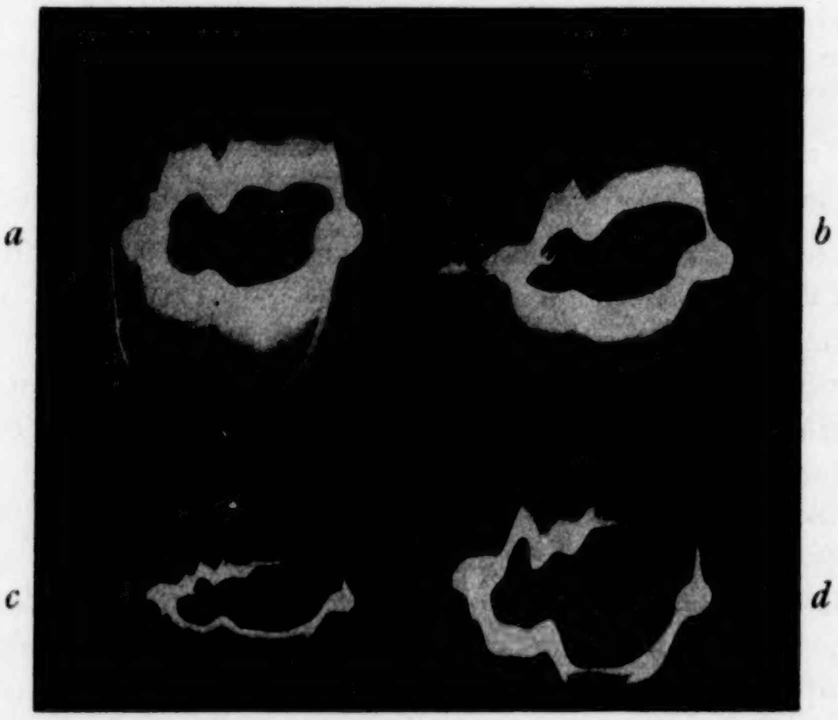

Fig. 2. Oszillogramme mit der Quecksilbertropfelektrode in 2*M* NaOH-Lösung, N_2-Atm., gegen ges. Kalomelelektrode: (a) Thiamin. HCl; (b) Cocarboxylase; (c) Thiamindisulfid; (d) Thiamin nach 5stündigem Kochen in 5*N* Salzsäure.

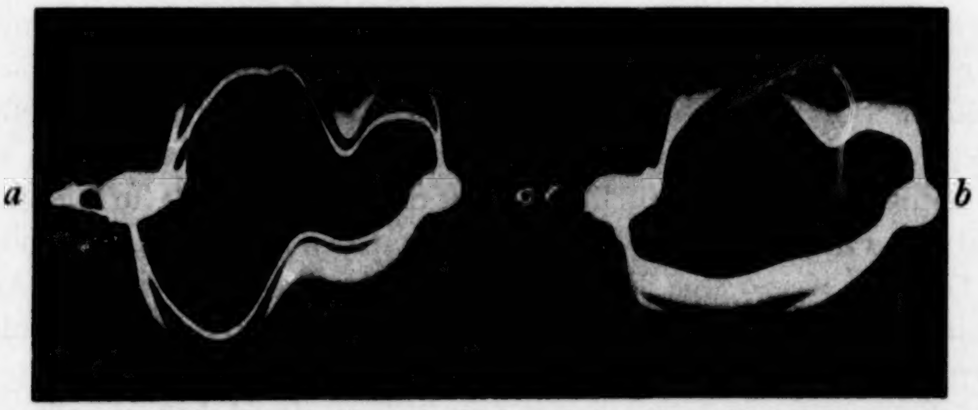

Fig. 3. Oszillogramme mit der Quecksilbertropfelektrode in 5%iger NaOH-Lösung, N_2-Atm., gegen ges. Kalomelelektrode: (a) 4-Methyl-5-(β-oxäthyl)-thiazol; (b) 2-Methyl-4-amino-5-äthoxymethyl-pyrimidin.

groskopisch und schmilzt etwa bei 270° unter Zersetzung. Der Stoff selbst lumineszíert ebenso wie seine methanolische, äthanolische und alkalische wässrige Lösung im UV-Licht gelbgrün, durch Ansäuern wird die Lumineszenz ausgelöscht. Das ultraviolette Absorptionsspektrum ähnelt sehr dem Spektrum des Tiamins, die in 8 mg%iger äthanolischer Lösung gemessenen Werte bilden auf der Durchlässigkeitskurve ein Minimum bei 234 mμ, ein Maximum bei 257 mμ, und ein zweites Minimum bei 277 mμ. In saurer Pufferlösung liefert dieser Stoff eine kathodische polarographische Stufe von Diffusionscharakter. Ihr Halbstufenpotential $E_{\frac{1}{2}}$ verschiebt sich beim Anstieg des pH-Wertes von 3.4 bis 7.55 zu negativeren Werten in den Grenzen von —1.21 bis —1.53 V gegen die gesättigte Kalomelelektrode. Diese Verschiebung ist linear und beträgt im Durchschnitt 84 mV pro pH-Einheit. Mit dem Anstieg des pH-Wertes verkleinert sich allmählich die Höhe der Stufe und gleichzeitig wird sie weniger ausgeprägt, bis sie bei pH >7.5 praktisch zu verschwinden beginnt (Fig. 4).

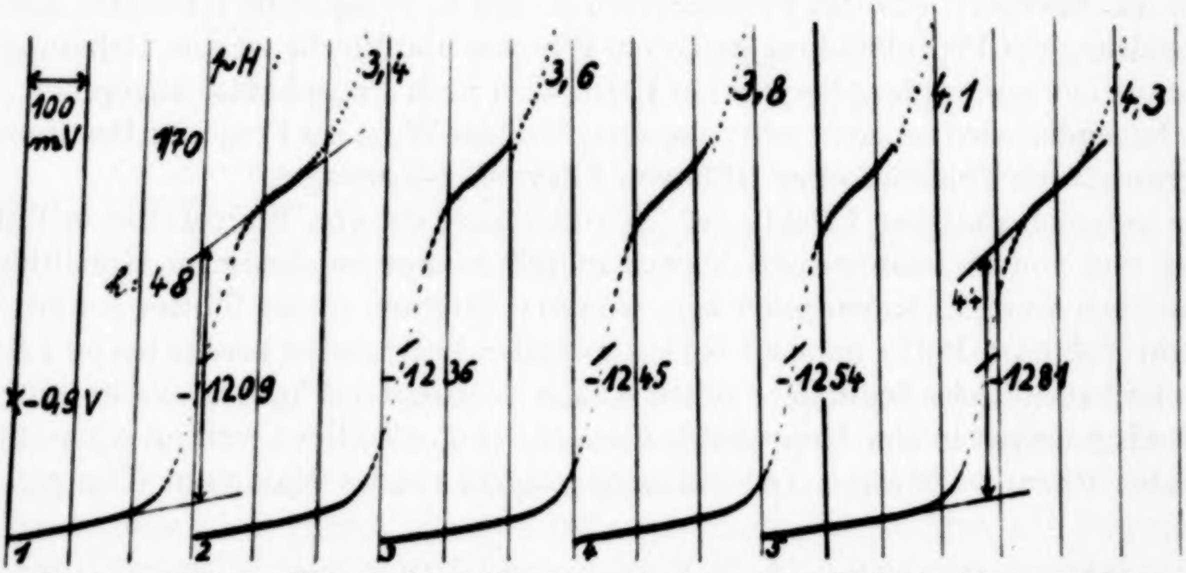

Fig. 4. Polarographische Kurven des gelbgrün lumineszierenden Thiaminabbauproduktes. Das Produkt (aus Thiamin durch Behandlung mit 30%igem Perhydrol in alkalischem Milieu gewonnen) in Abhängigkeit vom pH polarographiert. Kathodische Polarisation von —0.9 V an, Galv. Empf. 1/70, 2-V-Akku., gegen ges. Kalomelelektrode. Als Grundelektrolyt wegen der gleichzeitigen oszillographischen Untersuchung *ca.* 10-mal konzentriertere Acetat-Pufferlösung nach Walpol verwendet.

Auf den oszillographischen Kurven $\frac{dV}{dt} = f_1(V)$ entstehen mit der Quecksilbertropfelektrode in saurem Milieu zwei scharfe, erheblich negative kathodische Einschnitte, während die anodische Halbperiode keine Depolarisationswirkungen aufweist (Fig. 1a).

Ein ähnliches Oszillogramm liefert die Pyrimidin-Komponente des Thiamins, und zwar 2-Methyl-4-amino-5-äthoxymethyl-pyrimidin (Fig. 1b), während seine zweite Komponente, 4-Methyl-5-(β-oxäthyl)-thiazol, unter den gleichen Bedingungen ein wesentlich anderes Oszillogramm gibt. Da weiter die Maxima resp. Minima des ultravioletten Absorptionsspektrums des gelbgrün lumineszierenden Produktes bei sehr nahen Wellenlängen liegen wie die bekannten sauren Komponenten der Sulfitspaltung des Thiamins, ebenso wie auch anderer Amino- oder Oxy-Derivate des Methylpyrimidins[44], kann geschlossen werden, dass das bisher nicht identifizierte untersuchte Produkt den Pyrimidinkern enthält. Seine durch den drastischen alkalischen Perhydrolabbau der Thiazolkomponente des Thiamins bedingte Stabilität, weiter seine Elektroaktivität und schliesslich seine ausgeprägte gelbgrüne Lumineszens — zum Unterschied von der Reihe der blau lumineszierenden Stoffe von Thiochromstruktur — bilden den Gegenstand einer weiteren Untersuchung in analytischer Richtung.

ALKALISCHES PRODUKT DER COCARBOXYLASE

Bei der Bestimmung des Gesamt-Thiamins im natürlichen Material erfordert jede Modifikation der Jansenschen fluorometrischen Methode die völlige Befreiung dieses Vitamins aus seinen gebundenen Formen, denn in das Isobutanol wird nur das freie Thiochrom ausgeschüttelt. Das analoge Oxydationsprodukt der Cocarboxylase weist zwar gleichfalls eine blaue Lumineszens auf, bleibt jedoch in der gelben alkalischen Cyanoferrat(III)-Schicht zurück und wird nicht in das Isobutanol ausgeschüttelt. Die Befreiung des Thiamins wird durch schonende Hydrolyse mit Hilfe von zwei Enzymtypen durchgeführt. Für das Freimachen aus dem Eiweisskomplex benützt man die zur Spaltung der Peptidbindung geeignete Protease und für die weitere Befreiung des Thiamins aus seiner phosphorylierten Form wird noch Phosphatase zugegeben.

Im folgenden wird versucht, auf polarographischem Wege zur Frage der Bestimmung des gebundenen Thiamins ohne Hilfe von Enzymen beizutragen.

Die polarographischen Effekte der Cocarboxylase, die von Weidmann[8] in Pufferlösung und von Hamamoto und Yamanouchi[33] in ammoniakalischer Kobaltlösung beschrieben wurden, haben mich zum weiteren Studium dieses Stoffes geführt. Im Britton-Robinson-Puffer habe ich bei kathodischer Polarisation bereits bei pH 1.8 eine einfache katalytische Stufe der Cocarboxylase beobachtet (Fig. 5a), die im schwach alkalischen Gebiet in eine Doppelstufe übergeht (Fig. 5b). Etwa von pH 9.7 an bildet sich über ihrem positiveren Teil ein ausgeprägtes rundes Maximum (Fig. 5c). Mit

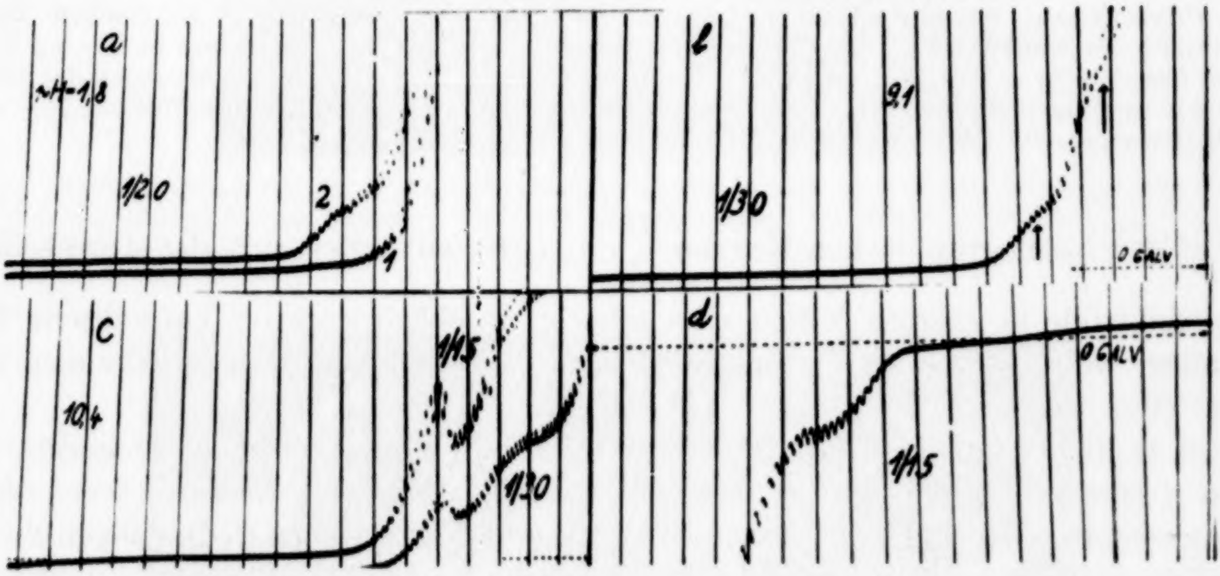

Fig. 5. Polarogramme der Cocarboxylase.
(a) Kurve (1): Britton-Robinson-Puffer vom pH 1.8. Kurve (2): Dieselbe Lösung mit Cocarboxylase in der Konzentration $5 \cdot 10^{-5} M$ bei Galv. Empf. 1/20.
(b) Derselbe Puffer vom pH 9.1 mit $10^{-3} M$ Cocarboxylase bei Empf. 1/30.
(c) Derselbe Puffer vom pH 10.4 mit $10^{-3} M$ Cocarboxylase bei Empf. 1/30 und 1/15.
(d) 5%ige NaOH-Lösung mit $10^{-3} M$ Cocarboxylase bei Galv. Empf. 1/15.
(a)-(c) kathodische Polarisation, (d) anodisch-kathodische Polarisation, gegenges. Kalomelelektrode.

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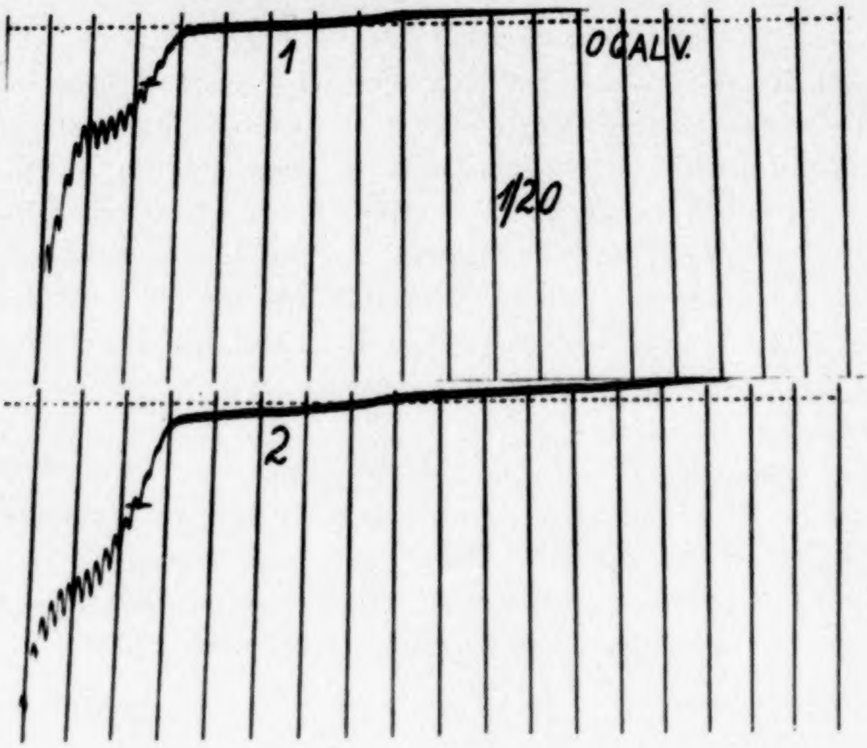

Fig. 6. Koinzidenz der Stufen der Cocarboxylase und des Thiamins.
Kurve (1): Cocarboxylase in 5%iger NaOH-Lösung.
Kurve (2): Zur Lösung der Kurve (1) weiter Thiamin zugegeben. Anodisch-kathodische Polarisation, gegen ges. Kalomelelektrode, Empf. 1/20, 2-V-Akku.

zunehmender Alkalität verringern sich diese kathodischen katalytischen Effekte, bis sie bei pH 11.5 völlig verschwinden. Gleichzeitig beginnt sich bei anodischer Polarisation etwa von pH 10.4 an eine kleine anodische Stufe zu zeigen, die mit steigendem pH-Wert höher wird, jedoch sehr gedehnt, wie eine wenig ausgeprägte Doppelstufe ist. Erst in einer 5%igen NaOH-Lösung liefert die Cocarboxylase eine entwickelte anodische Stufe (Fig. 5d), die mit der analogen Stufe des Thiamins koinzidiert (Fig. 6). Vergleichen wir in dieser Lösung weiter noch die oszillographischen Kurven, so ist sowohl beim Thiamin (Fig. 2a) als auch bei der Cocarboxylase (Fig. 2b) ein kathodischer und ein zu ihm reversibler anodischer Einschnitt sichtbar. Dieses charakteristische Paar reversibler Einschnitte 1 und 1' habe ich auch beim Thiamindisulfid festgestellt (Fig. 2c), bei den Systemen Cystin-Cystein, oxydiertes-reduziertes Glutathion und erheblich negativer verlagert beim 4-Methyl-5-(β-oxäthyl)-thiazol (Fig. 3a)*. Der entsprechende oszillographische mobile reversible Vorgang ist hier durch die Bildung eines Quecksilbersalzes mit den -SH- und -S-S-Stoffen an der Oberfläche der Tropfelektrode bedingt.

Von den Oszillogrammen des Thiamins, Thiamindisulfids und der Cocarboxylase (Fig. 2a, b, c) liegt die einfachste Kurve bei der Cocarboxylase vor. Es fehlt ihr der Einschnitt 3, der am ehesten der Pyrimidinkomponente zukommt, falls wir nämlich das Oszillogramm des 2-Methyl-4-amino-5-äthoxymethyl-pyrimidins in Fig. 3b beachten. Anscheinend gelangt es bei der Cocarboxylase infolge der komplexbildenden OH-Gruppen in der Pyrophosphat-Seitenkette zu einer Verzögerung der Elektrodenvorgänge und dadurch zu einer Vereinfachung der oszillographischen Kurve. Durch längeres Wiederholen der Elektrolyse entsteht bei der Cocarboxylase ebenso wie beim Thiamin nur ein einziger weiterer Einschnitt 2, der jedoch sofort zu Beginn der Elektrolyse beim Thiamindisulfid charakteristisch ist. Diese Beobachtungen sprechen dafür, dass die Cocarboxylase im alkalischen Milieu nicht Phosphorsäure abspaltet und dass sie folglich als phosphorylierte Thiolform anwesend ist, was weiter mit dem negatieven Jansenschen Thiochrom-Test in Übereinstimmung ist. Die so nachgewiesene polarographische Aktivität der Cocarboxylase bedeutet für die Bestimmung des Gesamtvitamins B_1 im natürlichen Material die Auslassung der enzymatischen Spaltung durch Phosphatasen.

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* In Übereinstimmung mit dem Zitat[16] habe ich bei dieser Verbindung in alkalischem Milieu keine polarographische anodische Stufe erhalten, offensichtlich wegen der ungenügenden Stabilität des entsprechenden Quecksilbersalzes.

Die weitere Befreiung des Thiamins, und zwar aus dem Eiweisskomplex, wird bei der Thiochrommethode, wie bereits erwähnt worden ist, durch schonende Hydrolyse mit Hilfe von Proteasen durchgeführt. Eine derartige Befreiung kann jedoch auch einfacher durchgeführt werden, und zwar durch drastischere Hydrolyse mit Säure bei erhöhter Temperatur. Trotz der verhältnismässig beträchtlichen Stabilität des Thia-

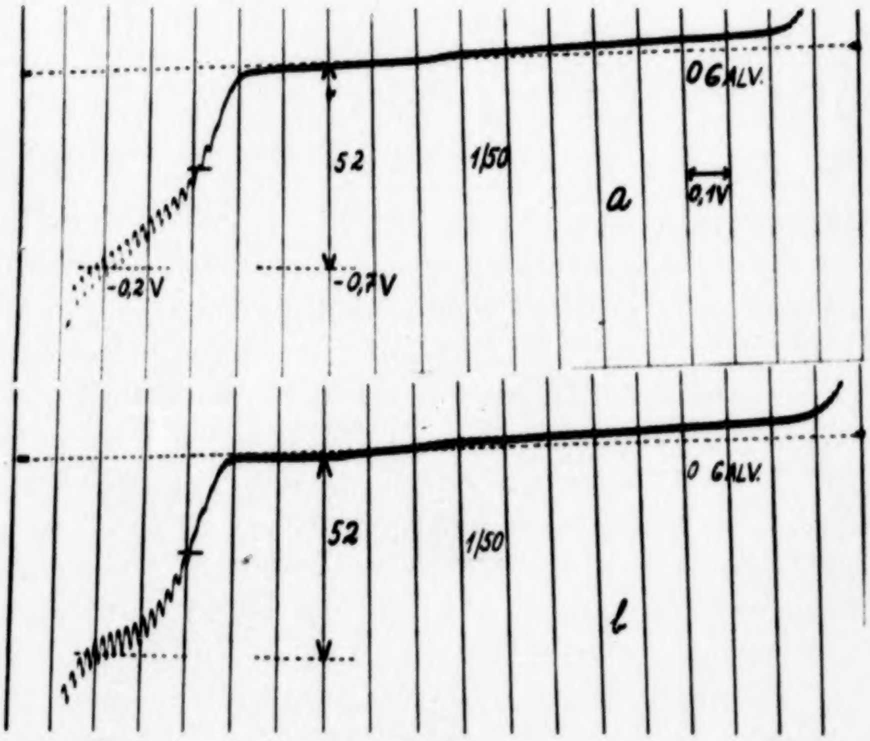

Fig. 7. Polarographische Kurven des Thiamins (a) vor der Hydrolyse, (b) nach der Hydrolyse durch 5stündiges Kochen in 5*N* Salzsäure.

Kurve (a) 2.5 ml 10*N* Salzsäure, 5 ml 10*N* NaOH, 30 ml H_2O vermischt und schliesslich 2.5 ml der Lösung I zugegeben. Die entstandene $3.75 \cdot 10^{-3} M$ Thiaminchlorid-hydrochlorid-Lösung in 0.625*M* NaCl und 0.625*N* NaOH in N_2-Atm. polarographiert bei Empf. 1/50, 2-V-Akku., kathodisch von 0 V an gegen ges. Kalomelelektrode.

Kurve (b) 30 ml H_2O mit 5 ml 10*N* NaOH und 5 ml der Lösung Ia. vermischt. Die entstandene Lösung von derselben analytischen Konzentration der Lösungskomponenten wie bei Kurve (a) unter denselben Bedingungen polarographiert.

Lösung I. : $6 \cdot 10^{-2} M$ Lösung von Thiaminchlorid-hydrochlorid.

Lösung Ia. : Die Lösung I im Verhältnis 1:1 mit *ca.* 10*N* (konz.) Salzsäure vermischt und unter Rückflusskühlung auf dem siedenden Wasserbad 5 Stunden lang gekocht.

Die Höhen der polarographischen Stufen in beiden Fällen gleich (52 mm), während mit der Jansenschen fluorometrischen Thiochrommethode wird eine Abnahme von 64% Thiamin durch hydrolytisch-thermische Einwirkung festgestellt.

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mins in saurem Medium macht sich in diesem Fall jedoch hauptsächlich die thermische Zersetzung geltend und die Thiochrommethode liefert erheblich niedrigere Werte. Demgegenüber sind die polarographischen Feststellungen überraschend, die zeigen, dass das Thiamin polarographisch sogar nach 5stündigem Kochen in 5*N* (16%iger) Salzsäure bestimmt werden kann. Bei der Ausmessung der Kurven bei gleichen Potentialen am Diffusionsstrom finden wir, dass eine derart hydrolysierte Lösung nach dem Alkalisieren eine anodische Stufe von derselben Höhe liefert, wie eine äquimolare Thiaminlösung, die nicht hydrolysiert wurde (vgl. die Kurven a, b in Fig. 7). Die polarographischen Kurven des Thiamins nach der Hydrolyse sind sogar etwas ausgeprägter (Kurve b in Fig. 7) als bei frisch bereiteten Thiaminlösungen (Kurve a in Fig. 7). Ähnlich zeigt sich auch ein geringerer Unterschied auf den Oszillogrammen, wo der anodische Einschnitt nach der Hydrolyse des Thiamins seine Steilheit verliert und der kathodische Reflex in stärkerem Mass zur Geltung kommt (Fig. 2d).

Durch das lange Kochen in Salzsäure entstehen folglich aus dem Thiamin andere Formen, die alle nach Alkalisierung bei praktisch gleichen Potentialen anodisch depolarisieren und praktisch die gleichen Diffusionskonstanten besitzen, so dass sich auch ein drastischer saurer hydrolytischer Eingriff nicht quantitativ polarographisch äussert — zum Unterschied von der Thiochrombestimmung.

In Verbindung mit Chromatographie oder einer anderen Technik einer geeigneten Konzentrierung des Vitamins und Entfernung des Balastüberschusses scheint die Bestimmung des gebundenen Vitamins B_1 ohne Hilfe von Enzymen durchführbar zu sein.

ZUSAMMENFASSUNG

Der Autor studiert oszillopolarographisch neue elektroaktive Formen des Thiamins und der Cocarboxylase und weist auf ihre analytische Anwendung hin. Als Beitrag zur Bestimmung des Thiamins in Arzneimitteln wird die Untersuchung eines neuen gelbgrün lumineszierenden Abbauproduktes gebracht, das aus dem Thiamin durch Einwirkung von 30%igem H_2O_2 oder Na_2O_2 in stark alkalischem Milieu entsteht. Aus dem weiteren Studium der Stabilität des Thiamins und der Elektroaktivität der Cocarboxylase ergeben sich Perspektiven für die Bestimmung des gebundenen Vitamins B_1 in natürlichem Material auf nichtenzymatischem Wege.

SUMMARY

The author has studied new electro-active forms of thiamin and cocarboxylase by means of oscillopolarography, and points out their analytical application. As contribution to the determination of thiamin in medicines, research was done on a new yellow-green luminescent degradation product formed on treating thiamin with 30% H_2O_2 or Na_2O_2 in strong alkaline solution. Further study of the stability of thiamin and the electro-activity of cocarboxylase offers new prospects for the non-enzymic determination of bound vitamine B_1 in natural materials.

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ANWENDUNGSMÖGLICHKEITEN DER HOCHFREQUENZMESSTECHNIK IN DER ANALYTISCHEN CHEMIE

von

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In der folgenden Arbeit wird unter den analytischen Anwendungsmöglichkeiten der Hochfrequenzmesstechnik die Bestimmung von Dielektrizitätskonstanten (DK), dielektrischen Verlusten (DV) und Hochfrequenzleitfähigkeiten (LF) verstanden. Dabei interessiert in den seltensten Fällen der absolute Betrag der Grössen. Vielmehr wird bei dieser Analysentechnik überwiegend auf Relativmessungen zurückgegriffen, bzw. das Messgerät unmittelbar in der analytisch interessierenden Grösse geeicht.

I. ALLGEMEINE APPARATIVE UND METHODISCHE ANGABEN

Für die beschriebenen Untersuchungen wurde ein Messgerät benutzt, welches einen einstufigen Quarz-Oszillator darstellt. Der Grossteil der Messungen wurde mit einer Frequenz von 7 MHz durchgeführt, obwohl grundsätzlich die Möglichkeit besteht, durch Steckspulen und Steckquarze einen raschen Frequenzwechsel vorzunehmen. Das Gerät kam in zwei verschiedenen Ausführungsformen zur Anwendung, deren Unterschiede aus Fig. 1 hervorgehen.

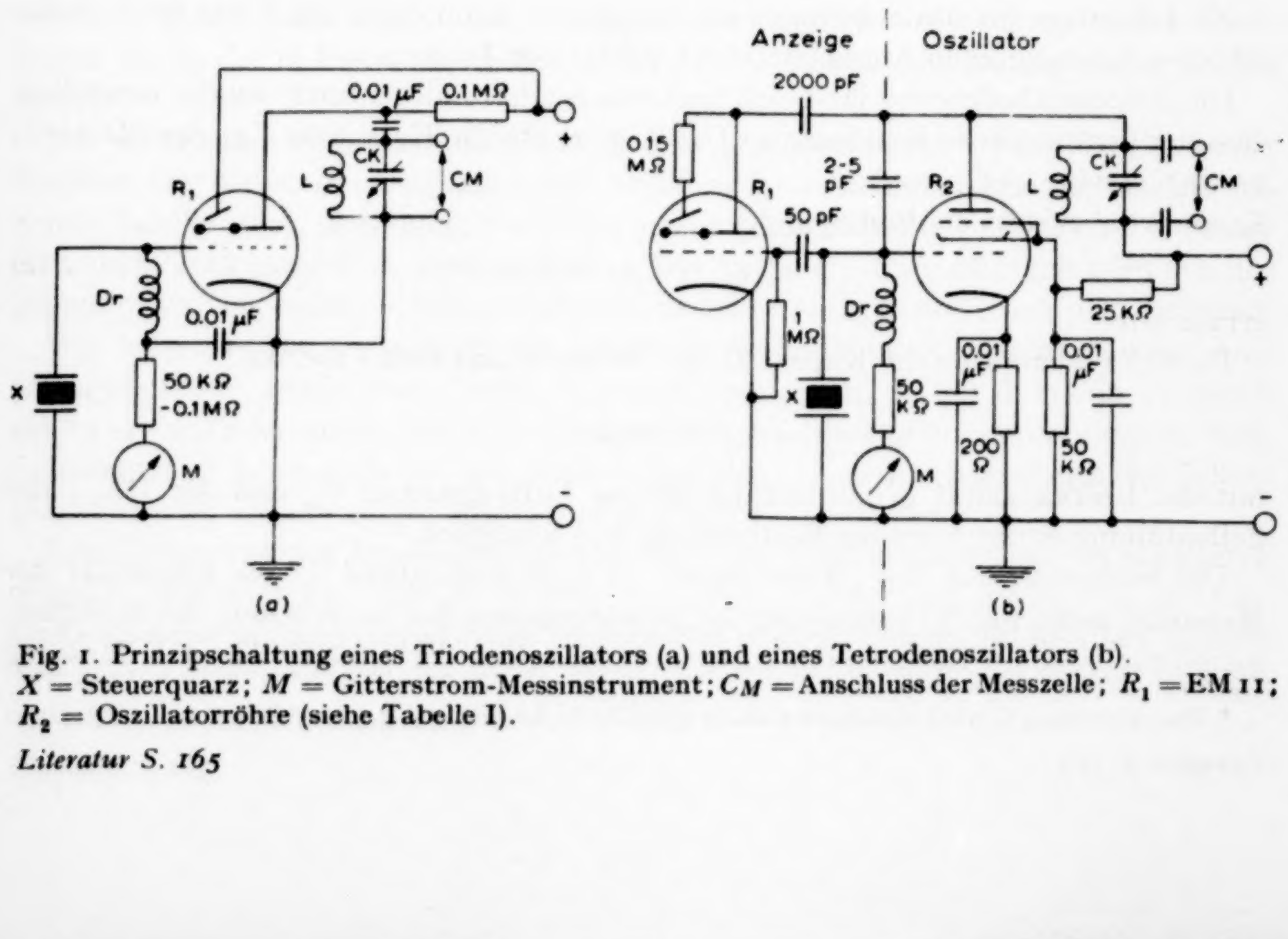

Fig. 1. Prinzipschaltung eines Triodenoszillators (a) und eines Tetrodenoszillators (b). X = Steuerquarz; M = Gitterstrom-Messinstrument; C_M = Anschluss der Messzelle; R_1 = EM 11; R_2 = Oszillatorröhre (siehe Tabelle I).

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Beim Triodenoszillator wird das „magische Auge" gleichzeitig zur Schwingungserzeugung und Resonanzanzeige benutzt[1,2,3]. Der Tetrodenoszillator dagegen lässt die Trennung von Oszillator- und Anzeigeteil zu. Die sich daraus ergebenden Vorteile bei Anwendung der Gitterstrommesstechnik werden noch näher beschrieben.

So einfach die Schaltung in ihrem Aufbau ist, so vielseitige Anwendungsmöglichkeiten ergeben sich dennoch, wobei ein weiterer Vorteil in einer hohen Betriebssicherheit des Gerätes liegt. Es sind grundsätzlich zwei verschiedene Bedienungsarten möglich:

(1) Die Kompensationsmethode,
(2) die Ausschlagsmethode.

Die Arbeitsweise der *Kompensationsmethode* wird leicht verständlich, wenn man sich vergegenwärtigt, dass im Resonanzfall gilt:

$$\text{Quarzfrequenz} = \text{Anodenkreisfrequenz} = \frac{1}{2\pi\sqrt{LC_{\text{res}}}} \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

mit $C_{\text{ges}} = C_{\text{res}}$.

Bei Anschluss einer Messzelle der Kapazität C_M wird $C_{\text{ges}} > C_{\text{res}}$, der Kreis ist damit verstimmt und der Oszillator schwingt nicht mehr.

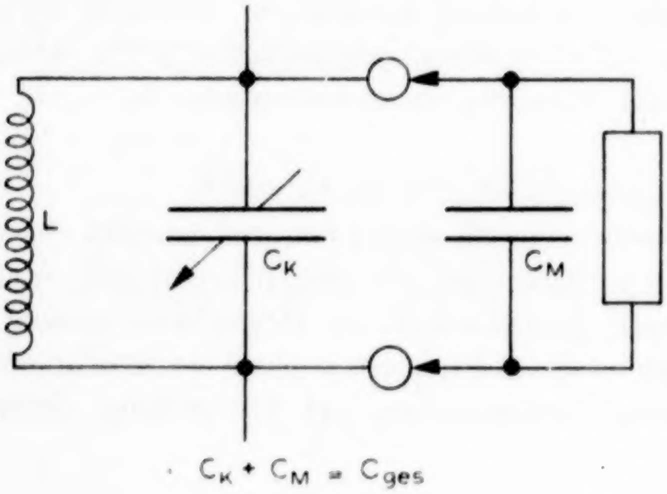

Fig. 2. Aufbau eines Schwingungskreisess. L = Induktivität; C_K = veränderliche Kapazität (Drehkondensator); C_M = Messzelle mit Ableitung G.

Als Kriterium für das Schwingen des Oszillators kann dabei die Form der Leuchtsektoren des magischen Auges bzw. der Gitterstrom J_G dienen.

Die Resonanzbedingung lässt sich im vorliegenden Fall dadurch wieder herstellen, dass der veränderliche Kondensator C_K (Fig. 2) um die Kapazität C_M der Messzelle verringert wird: $\triangle C_K = C_M$.

Es muss dabei stets die Bedingung

$$C_{\text{res}} = C_K + C_M \quad \ldots\ldots\ldots\ldots\ldots \quad (2)$$

erfüllt sein.

Da sich andererseits die Kapazität der Messzelle aus dem Produkt

$$C_M = \varepsilon \cdot C_0$$

mit der Leerkapazität (Vakuumkapazität ≈ Luftkapazität) C_0 und der DK ε der Zellenfüllung ergibt, wird die Bestimmung von ε möglich.

Das Vorhandensein von „Ableitungen" (Parallelwiderstand G* zur Kapazität der Messzelle, siehe Fig. 2) beeinflusst die Messergebnisse bei Anwendung der Kompensationsmethode im Rahmen der Anwendungsgrenzen der analytischen DK-Messung

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* Die Ableitung G wird üblicherweise als spezifische Leitfähigkeit χ angegeben.

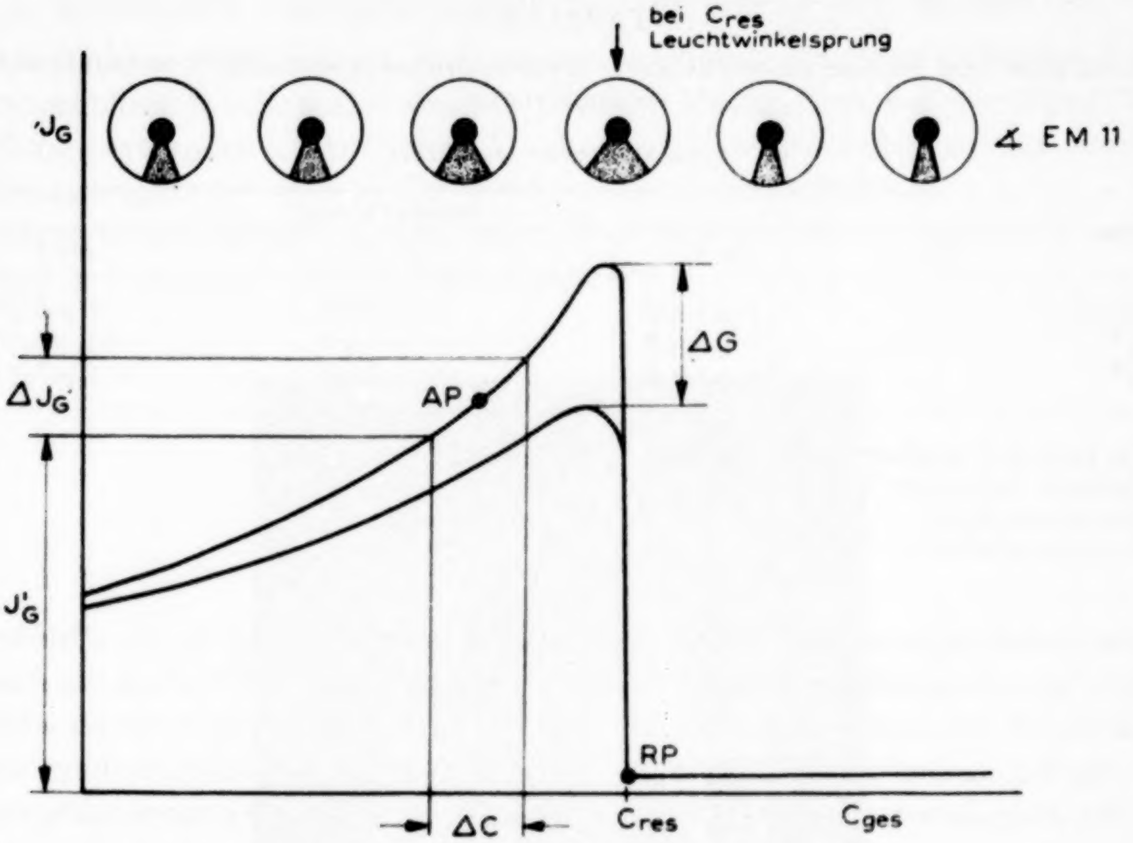

Fig. 3. Gitterstrom-Charakteristik eines Quarzoszillators nach Fig. 1.
RP = Resonanzpunkt (Abstimmkriterium der Kompensationsmethode); *AP* = Arbeitspunkt bei Anwendung der Ausschlagsmethode; J_G = Gitterstrom; $\triangle G$ = Abnahme des maximal fliessenden Gitterstromes durch die Ableitung *G* (siehe Fig. 2).
∡ *EM* 11 = schematisierte Leuchtwinkelform des magischen Auges.

praktisch nicht. Das Verfahren setzt jedoch eine manuelle Anstimmung des DK-Meters voraus und lässt somit keine registrierenden Messungen zu.

Das Prinzip der *Ausschlagsmethode* wird durch Fig. 3 veranschaulicht. Hieraus wird ersichtlich, dass stets dann der Oszillator schwingt und folglich ein kräftiger Gitterstrom J_G fliesst, wenn $C_{\text{ges}} < C_{\text{res}}$. Es ergibt sich somit ein Schwingbereich des Oszillators, der in der in Fig. 3 angegebenen Art für DK-Messungen herangezogen werden kann[4,5].

Die erzielbare Ansprechempfindlichkeit der Ausschlagsmethode hängt stark von der Steilheit der benutzten Oszillatorröhre und von ihrer Betriebsspannung ab. Die folgende Tabelle zeigt, dass dabei Pentoden in Tetrodenschaltung (siehe Fig. 1 b) besonders vorteilhaft eingesetzt werden können. Die Ansprechempfindlichkeit wird von uns allgemein auf das steilste Stück der Gitterstromkurve bezogen und in μA/pF angegeben.

Wir halten es für vorteilhaft, die Ansprechempfindlichkeit aller nach einer Ausschlagsmethode arbeitenden Geräte in μA/pF anzugeben, da nur dann ein Vergleich der zu erwartenden analytischen Leistungen verschiedener Gerätetypen möglich wird. Grundsätzlich kann jede der hier interessierenden Grössen entsprechend der Zellencharakteristik als kapazitive Komponente ausgedrückt werden.

Eine Steigerung der Ansprechempfindlichkeit der Ausschlagsmethode wird dadurch möglich, dass nach Fig. 3 die nicht interessierende „Grundkomponente" J'_G des Gitterstromes durch einen Gegenstrom kompensiert wird und nunmehr die allein interessierenden Gitterstrom*änderungen* $\triangle J_G$ bei erhöhter Empfindlichkeit des Anzeigeinstrumentes zur Messung kommen[5].

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TABELLE I

VERGLEICH DER GITTERSTROMSTEILHEIT (ANSPRECHEMPFINDLICHKEIT) VERSCHIEDENER OSZILLATOREN

Quarzfrequenz = 7 MHz

Röhre	*Betriebsspannung*		
	200 V	*300 V*	*400 V*
1/2 ECC 82	7 μA/pF	12 μA/pF	17 μA/pF
6 SK 7*	37 μA/pF	52 μA/pF	65 μA/pF
6 AC 7*	65 μA/pF	110 μA/pF	175 μA/pF

* Als Tetroden geschaltet, d.h. G_2 und G_3 verbunden.
Maximal fliessender Gitterstrom:
Triodenoszillator: 300-500 μA;
Tetrodenoszillator: 1-2 mA.

Diese Ausschlagsmethode wurde von uns mit bestem Erfolg für verschiedene Registrierungen chemischer und biologischer Vorgänge eingesetzt[6,7]. Dass die Ansprechcharakteristik des Gerätes dabei nicht-linear ist, dürfte selten stören, da ohnehin meist durch die Eigenschaften der Messzelle ein nichtlineares Ansprechen bedingt wird[8]. Je nach der Aufgabenstellung ergeben sich folgende apparative Voraussetzungen:

TABELLE II

APPARATIVE VORAUSSETZUNGEN EINER REGISTRIERTECHNIK NACH DER AUSSCHLAGSMETHODE

Zeitlicher Ablauf des interessierenden Vorganges	*Prinzip der Anzeige*	
	*Direktanzeige**	*Anzeige nach Verstärkung**
Langsam	Punktschreiber	Linienschreiber
Schnell	Spiegelgalvanometer mit Phototrommel	Schleifen-Oszillograph

Voraussetzung für ein verlässliches Arbeiten der Ausschlagsmethode unter Messung des Gitterstromes ist eine sehr gute Stabilisation der Betriebsspannungen des Oszillators (Anodenspannung und Heizspannung), was jedoch ohne Schwierigkeiten mit den üblichen Mitteln erreicht werden kann.

Während die Ergebnisse der Kompensationsmethode durch das Auftreten von Ableitungen (Fig. 2) kaum gestört werden, tritt bei der Ausschlagsmethode eine starke Beeinflussung des Gitterstromes auf (Fig. 3). Das ist stets zu beachten, da anderenfalls — besonders im Falle von wässrigen oder alkoholischen Lösungen — starke Messwertverfälschungen zustandekommen können[10]. Andererseits ergibt sich durch Bestimmung des maximal fliessenden Gitterstromes nach Fig. 3 eine Möglichkeit, den Betrag der Ableitung G zu bestimmen[5]. Wenn gleichzeitig die Kapazität C der Messzelle nach der Kompensationsmethode ermittelt wird, lässt sich der „Ableitungsverlust" der Messzelle aus der Beziehung

$$\mathrm{tg}\,\delta = \frac{G}{\omega C} \quad \ldots\ldots\ldots\ldots \quad (3)$$

berechnen.

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2. BAUFORMEN UND ELEKTRISCHE EIGENSCHAFTEN VON MESSZELLEN

Im Abschnitt 1 wurde gezeigt, dass einstufige Quarzoszillatoren vielseitige Anwendungsmöglichkeiten zulassen, wobei die gewählte Messtechnik der jeweiligen Aufgabenstellung anzupassen ist. In diesem Abschnitt soll hervorgehoben werden, dass ähnliche Anpassungsfragen auch in der Wahl der Messzellen auftreten.

Die folgende Tabelle gibt zunächst einen Überblick über die wichtigsten Messzellenarten und ihre messtechnischen Eigenschaften[6,8].

Fig. 4. Grössenverhältnisse und Ausführungsbeispiele für Formkörper aus Condensa F mit aufgebrannten Silberelektroden.

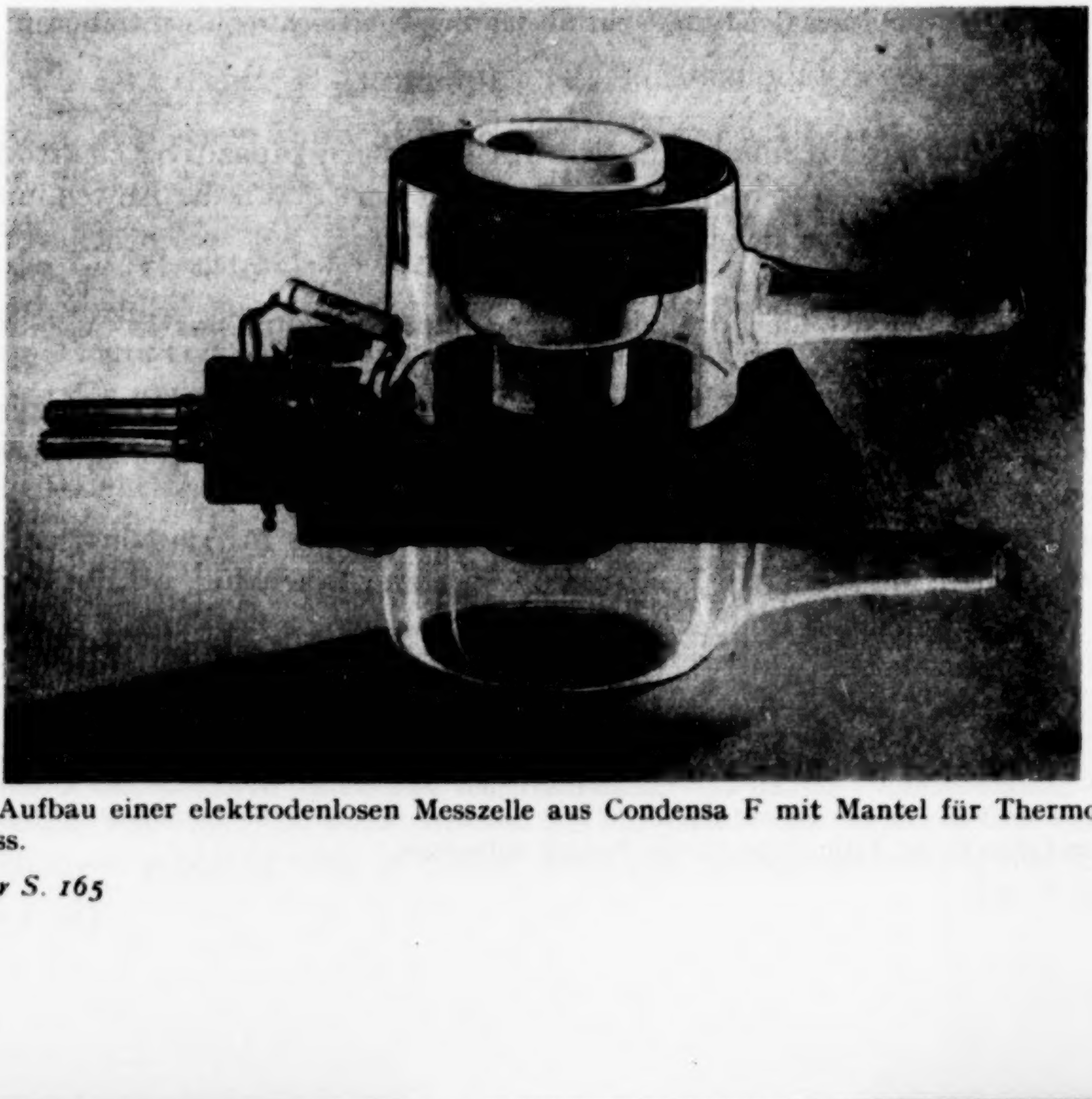

Fig. 5. Aufbau einer elektrodenlosen Messzelle aus Condensa F mit Mantel für Thermostatenanschluss.

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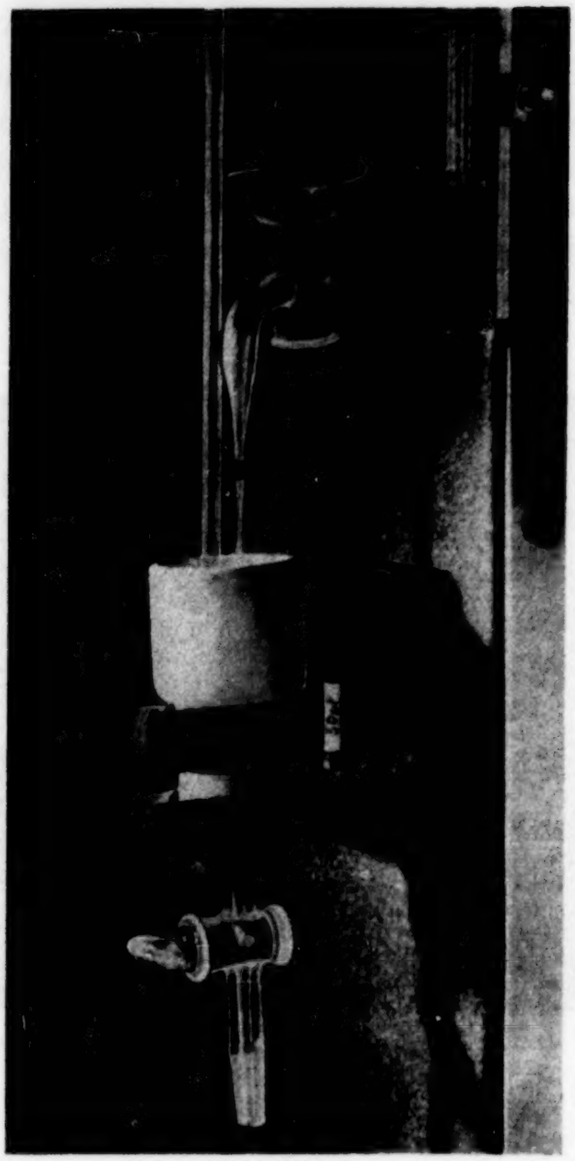

Fig. 6. Messzelle aus Condensa F zur Ausführung von Hochfrequenztitrationen.

Hier soll näher nur auf einige praktische Ausführungen kapazitiver elektrodenloser Messzellen* eingegangen werden, da wir diese Zellenart durch die Anwendung eines keramischen Werkstoffes hoher DK (Condensa F, $\varepsilon = 80$) wesentlich verbessern konnten[11].

Fig. 4 zeigt zunächst die Formkörper aus Condensa F mit *aussen* aufgebrannten lötfähigen Silberelektroden.

Der Substanzbedarf der Zelle beträgt etwa 8 ml und die Ansprechempfindlichkeit ist etwa 12 mal grösser als die einer Glaszelle gleicher geometrischer Abmessungen.

Diese Formkörper wurden speziell für die LF-Messung in Ampullen entwickelt, wobei die Notwendigkeit einer Temperierung bestand. Nach Fig. 5 kann das in einfacher Weise durch einen Doppelmantel erreicht werden, der an einen Paraffinölthermostaten angeschlossen wird[5,12]. Wasser scheidet infolge seiner ungünstigen dielektrischen Eigenschaften als Temperierflüssigkeit aus.

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* Als ,,elektrodenlos'' werden Zellenkonstruktionen bezeichnet, welche keinen unmittelbaren Kontakt zwischen der *aussen* auf der Zelle angebrachten Messstrecke (Kondensatorbeläge oder Spule) und dem in der Zelle vorhandenen Mesgut aufweisen.

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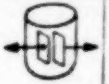
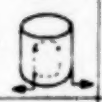
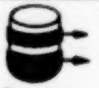
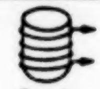
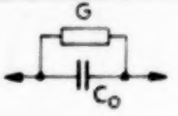
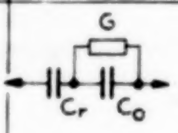
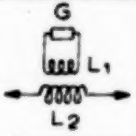
TABELLE III

BAUFORMEN UND ERSATZSCHALTUNGEN VERSCHIEDENER MESSZELLENARTEN

Prinzip	Zelle mit Flussigkeitskontakt	Elektrodenlose Messzellen	
		kapazitive	induktive
Bauform (schematisch), praktische Ausführung s. 42	Plattenkondensator  Zylinderkondensator 	 Beläge und Spule aussen auf der Messzelle	
Ersatzschaltbild:			
Ansprechen der Zellen auf.	DK (ε); (Ableitung G wird nur bei Abstimmen auf Gitterstrommaximum erfasst)	DK (ε) und LF (χ) (getrennte Auswertung nach[13] moglich)	

Schliesslich konnten wir die Formkörper auch mit bestem Erfolg für Hochfrequenztitrationen einsetzen. Nach Fig. 6 wird hierzu der Boden der Zelle abgeschliffen. Eine federnde Halterung ermöglicht einen leichten Wechsel der Zellen für Reinigungszwecke.

Die Formkörper lassen sich auch in der Ausführung mit abgeschliffenem Boden für die verschiedensten Zwecke bei Durchflussmessungen heranziehen, wie der praktische Aufbau der Messzelle eines „elektrodenlosen CO_2-Schreibers" zeigt (Fig. 7)[7].

3. ANALYTISCHE ANWENDUNGEN DER HOCHFREQUENZMESSTECHNIK

Die vorangegangenen Betrachtungen über die Eigenschaften der Messzellen liessen erkennen, dass in Abhängigkeit von der Art der Zelle eine Beeinflussung ihrer Leerkapazität C_0 durch eine Änderung der DK (ε) oder ihrer Ableitung G durch eine Änderung der LF (χ) zustandekommt. Dabei können beide Grössen auch gleichzeitig erfasst werden, sodass eine messtechnische Trennung notwendig wird[13]. Es ist nun analytisch von Wichtigkeit, zu erkennen, welche Zusammenhänge zwischen C_0 und G bzw. den Grössen ε und χ und der Zusammensetzung eines analytisch interessierenden Systems bestehen. Die funktionellen Verknüpfungen sind dabei nur in seltenen Fällen linearer Art, sodass sich meist eine empirische Auswertung an Hand von Eichreihen notwendig macht[3]. Diese Forderung entfällt jedoch dann, wenn (relative) Reinheitskontrollen durchgeführt werden sollen und verlässliche Standardpräparate verfügbar sind[3]. Der absolute Betrag von ε, χ und tg δ interessiert bei diesen Messungen nur selten.

Die analytischen Anwendungsmöglichkeiten hochfrequenztechnischer Messmethoden wurden bereits in den 30er Jahren auf der Seite der DK-Messung erkannt[14,15], während die LF-Messung mit Hochfrequenz konsequent erst nach Schaffung der elektrodenlosen Messtechnik bearbeitet wurde[16,17]. Die auf diesen Gebieten liegenden analytischen Möglichkeiten haben in den letzten Jahren eine solche Fülle von Veröffentlichungen gebracht, dass in diesem Abschnitt im Zusammenhang mit den den

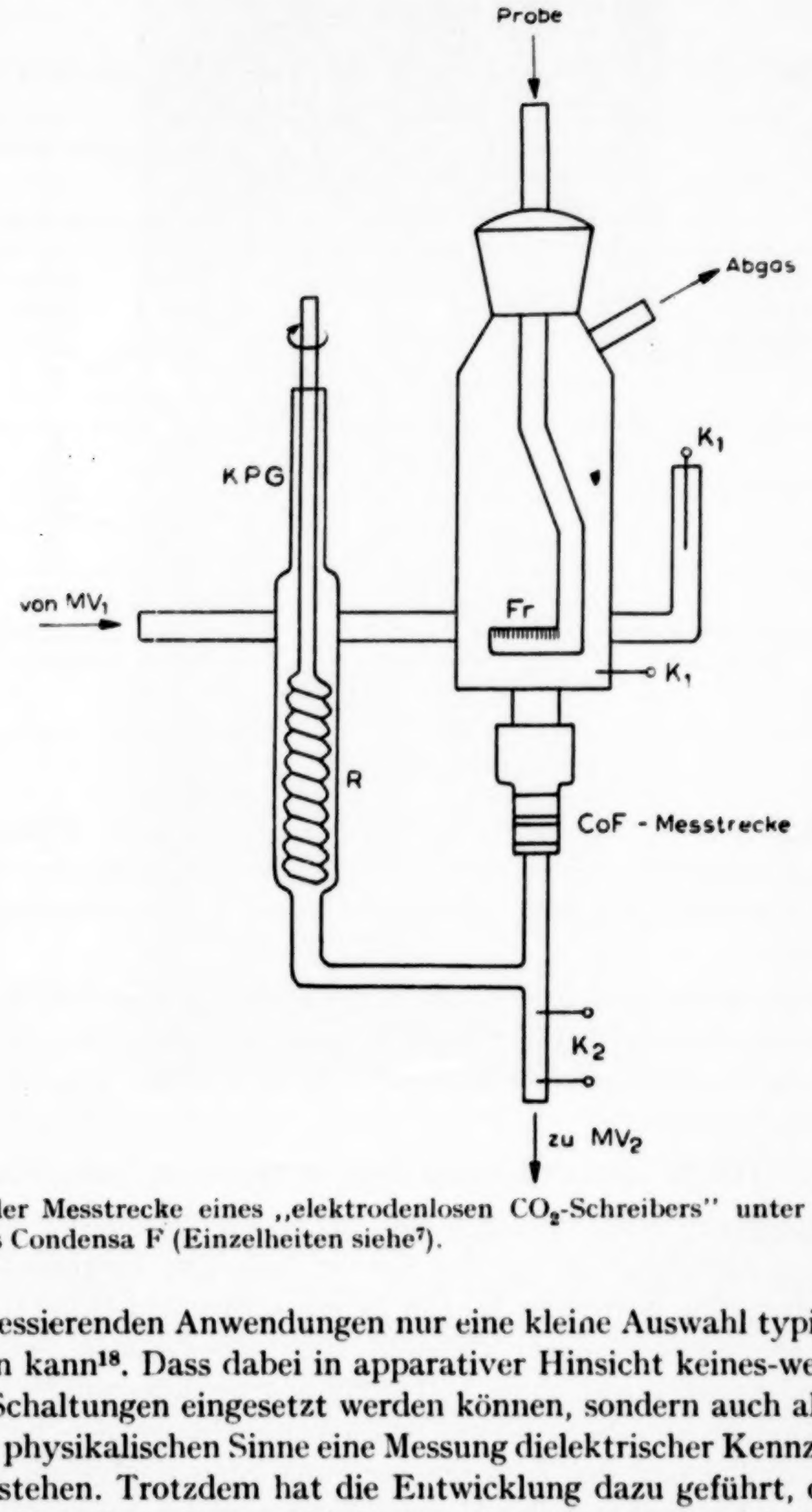


Fig. 7. Aufbau der Messtrecke eines „elektrodenlosen CO$_2$-Schreibers" unter Verwendung von Formkörpern aus Condensa F (Einzelheiten siehe[7]).

Chemiker interessierenden Anwendungen nur eine kleine Auswahl typischer Beispiele gegeben werden kann[18]. Dass dabei in apparativer Hinsicht keines-wegs nur die hier besprochenen Schaltungen eingesetzt werden können, sondern auch alle anderen Geräte, welche im physikalischen Sinne eine Messung dielektrischer Kennzahlen zulassen, dürfte sich verstehen. Trotzdem hat die Entwicklung dazu geführt, dass speziell für die Zwecke des Chemikers die verschiedensten Gerätetypen entwickelt und die Messgenauigkeit in einigen Fällen bis an die Grenze des zur Zeit apparativ möglichen getrieben wurde.

3.1 Beispiele zur Anwendungsmöglichkeit von DK-Messungen in der analytischen Chemie

Analytische Aufgabe	*Anwendungsbeispiel*	*Literatur*
Reinheitskontrolle	Kontrolle der Reinigung von Diäthylaminoäthanol durch Destillation	19
	Nachweis der Verfälschung und Alterung ätherischer Öle	3
	Reinigung von Benzol für DK-Eichungen	20

Fortsetzung

Analytische Aufgabe	*Anwendungsbeispiel*	*Literatur*
Analyse binärer Systeme	Wasserbestimmungen:	
	1. In Flüssigkeiten:	
	Wasser in Glyzerin	21
	2. In Pulvern, Pasten u.ä.	
	2.1 direkte Methode	
	(Probe kommt als Pulver in die Messzelle)	3
	Wassergehalt von Stärke und Dextran	3, 22
	2.2 indirekte Methode	
	(Wasser wird mit Dioxan extrahiert)	3, 10
	Wassergehalt von Fleischwaren	23
	Analyse technischer Lösungsmittel	41
	Gehaltsbestimmung von Essigsäureanhydrid	3
	Bestimmung von Cyclohexanol in technischem Cyclohexanon	24
Analyse ternärer Systeme	Untersuchung des Systems Methanol/Methylazetat/Äthylazetat (Lösungsmittel E 13 der Chemischen Werke Buna)	41
	Bestimmung des γ-Isomeren in technischen Hexachlorcyclohexan-gemischen	25, 26
	Analyse von technischem DDT	27
Kinetische Untersuchungen	Auswertung der DK-Änderungen bei der Veresterung von Essigsäureanhydrid mit Alkoholen für kinetische Studien	28, 29

3.2 *Anwendungsbeispiele für analytische Anwendungen von DV-Messungen*

Analytische Aufgabe	*Anwendungsbeispiel*	*Literatur*
Reinheitskontrolle bzw. Typenanalyse	Identifizierung von Weichmachern durch Aufnahme der tgδ-Temperatur-Funktion	30
	Nachweis der Verfälschung von Erdnussöl durch höhere Fettsäuren	31
Analyse binärer Systeme	Wasserbestimmung in Benzol, Methanol und Homologen	31
	Bestimmung der Carbonylgruppen in Polyäthylen	32

3.3 *LF-Messungen mit Hochfrequenz (elektrodenlose Messungen) und ihre Einsatzmöglichkeiten*

Das Gebiet der konduktometrischen Analyse an Hand von LF-Messungen kann in sehr vielen Fällen sowohl unter Anwendung „klassischer LF-Messungen" (mit Niederfrequenz) als auch der „elektrodenlosen Methode" (mit Hochfrequenz) durchgeführt werden. Der Aussageinhalt wird nur dann unterschiedlich, wenn zwischen dem niederfrequenten und hochfrequenten Gebiet die LF Dispersionserscheinungen zeigt, was besonders bei der Untersuchung hochpolymerer Lösungen zu berücksichtigen ist.

Eindeutige Vorteile weist die elektrodenlose LF-Messtechnik stets dann auf, wenn es gilt, die bei der klassischen Methode möglichen Adsorptionserscheinungen an den

Elektroden bei Messung hochverdünnter Lösungen zu vermeiden oder die Gefahr einer Elektrodenvergiftung oder Verunreinigung auszuschalten[17].

Grundsätzliche neue Anwendungsgebiete erschliessen sich der elektrodenlosen Messtechnik dadurch, dass es möglich wird, durch die Wandung nicht-metallischer Behälter hindurch die LF des Inhaltes zu bestimmen[11,13]. Dieser Möglichkeit kommt besondere Bedeutung in der Biochemie, Pharmazie und Mikrobiologie zu, wenn es etwa gilt, unter Wahrung der Sterilität in Ampullen oder Kulturgläsern Messungen durchzuführen.

Analytische Aufgabe	*Anwendungsbeispiel*	*Literatur*
Reinheitskontrolle	Bestimmung des Salzgehaltes von Speisewasser für Hochdruckkessel	34
	Prüfung der Entsalzung von dialysierten Serumfraktionen; Messung der bereits in Ampullen eingeschmolzenen Proben zur Betriebskontrolle	12
Wasserbestimmung	Wasserbestimmung in Ammoniumnitrat durch Extraktion met einem Dioxan – Methanol-Gemisch	35
Kinetik von Stoffwechselvorgängen und Fermentreaktionen	Bestimmung der Ureaseaktivität von Mikroorganismen	7
Endpunktanzeige bei Titrationen (Hochfrequenztitrationen)[8,36,37]	Simultanbestimmung von Chlorid und Sulfat im Meerwasser	38
	Komplexometrische Bestimmung verschiedener Metalle	39
	Bestimmung von Aminosäuren und Peptiden in abgebauten Eiweisskörpern	40

ZUSAMMENFASSUNG

In der vorliegenden Arbeit wurde gezeigt, dass einstufige Quarzoszillatoren auf Grund ihrer hochfrequenztechnischen Eigenschaften für die Bestimmung von Dielektrizitätskonstanten, dielektrischen Verlusten und Hochfrequenzleitfähigkeiten herangezogen werden können. Dabei wird je nach der interessierenden Grösse die Messung nach einer Kompensations- oder Ausschlagsmethode durchgeführt. Hinsichtlich der verfügbaren Messzellen ergeben sich zahlreiche Anpassungsmöglichkeiten für Aufgabenstellungen der chemischen Analyse, indem meist empirische Zusammenhänge zwischen den genannten dielektrischen Kennzahlen und der Zusammensetzung chemischer Systeme gefunden werden. Eine Zusammenstellung neuerer analytischer Arbeiten schliesst die Übersicht über die Anwendungsmöglichkeiten der Hochfrequenzmesstechnik in der analytischen Chemie ab.

SUMMARY

It was shown that, on the basis of their properties as regards high-frequency technique, single-stage quartz oscillators can be used for the determination of dielectric constants, dielectric losses, and high-frequency conductivities. According to the properties to be measured, the measurements are carried out by a compensation method or a deflection method. In view of the measuring cells available, the technique can be applied in various ways to problems of chemical analysis, since relationships (mostly empirical) exist between the above-mentioned dielectric properties and the composition of chemical systems. A review of the possibilities of application of high-frequency measuring technique to analytical chemistry is given, as well as a collection of the most recent literature in this field.

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DISKUSSION

Dr. I. Epelboin (Paris):

On sait depuis fort longtemps que les mesures de la constante diélectrique, par une méthode de résonance ou par la méthode des doubles battements, sont très sensibles. Mais dans le cas des électrolytes ces mesures soulèvent de grandes difficultés car la constante diélectrique est une quantité complexe $\varepsilon' - \gamma\varepsilon''$ et les mesures précitées ne donnent pas la constante diélectrique ε' mais une valeur relative qui dépend de $\varepsilon' - \gamma\varepsilon''$, de la distortion des lignes de courant dans le condensateur et de la structure de la double couche électrochimique.

Ir. F. Oehme:

Resonanzschaltungen können bei DK-Messungen bei niederen Frequenzen infolge von Feldverzerrung fehlerhaft sein. Durch Eichung mit Flüssigkeitsgemischen (Dioxan/Wasser) lassen sich diese Fehler weitgehend ausschalten. Für analytische Arbeiten besteht diese Notwendigkeit nicht.

TITRIMÈTRE HAUTE FRÉQUENCE
UTILISATION POUR LES TITRAGES EN MILIEU ANHYDRE

par

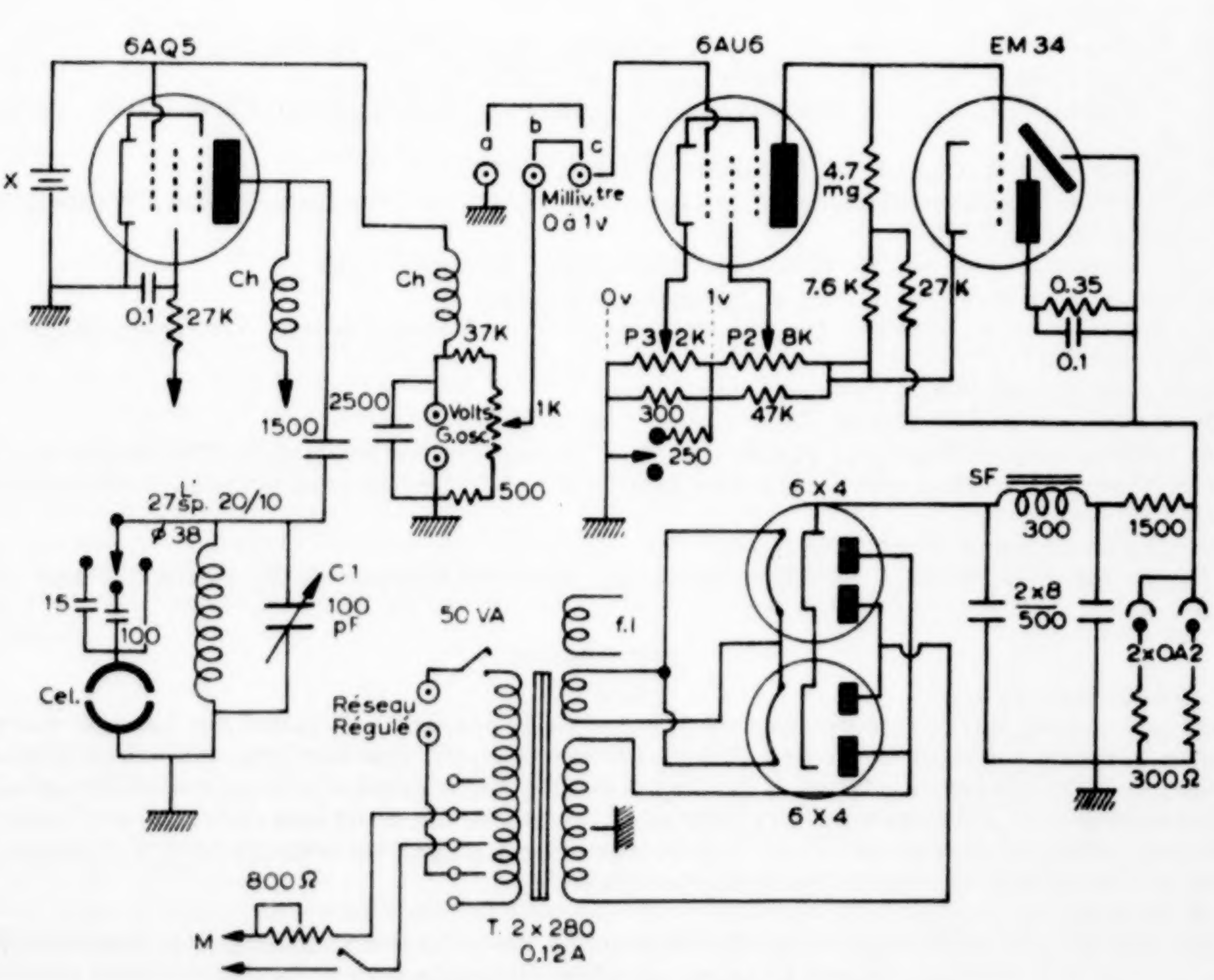
Y. CONSEILLER ET J. COURTEIX

Société des Usines Chimiques Rhône-Poulenc, Laboratoires de Recherches de l'Usine de Vitry s/Seine (France)

C'est depuis 1946 avec les travaux de FORMAN ET CRISP[1] et ceux de JENSEN ET PARRACK[2] qu'on relève dans la littérature des publications sur l'emploi de la technique haute fréquence en analyse.

Cette technique complète l'arsenal du chimiste analyste et étend ses possibilités dans le domaine des dosages en solvant anhydre où il est souvent délicat, sinon impossible, de trouver l'indicateur approprié.

Elle présente l'avantage de ne pas introduire d'électrode dans la solution et de pouvoir s'appliquer quelle que soit la résistance électrique du solvant.


6AQ5
6AU6
EM 34
X
a
b
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Milliv.tre
0 à 1v
Ch
0.1
27K
Ch
37K
1500
2500
Volts
G.osc
1K
500
4.7
mg
0v
1v
7.6 K
27K
P3
2K
P2
8K
300
47K
250
0.35
0.1
SF
300
1500
6 X 4
6 X 4
27 sp. 20/10
ø 38
C 1
100
pF
15
100
Cel.
50 VA
f.l
Réseau
Régulé
2x8
500
2xOA2
300Ω
800Ω
M
T. 2 x 280
0,12 A

Fig. 1. Titrimètre haute fréquence: schéma de principe.

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Les applications qui en ont été faites sont déjà nombreuses et l'on peut relever entre autres:

(a) Titrages d'acides organiques au méthylate en milieu benzène méthanol[3] ou en milieu diméthylformamide[4-6].

(b) Titrages des phénols ou des mélanges de phénol au méthylate[7].

(c) Titrage de bases organiques à l'acide perchlorique en milieu acétique[8,9,5,6].

(d) Dosage des traces d'eau.

Les appareils utilisés sont très variés[10,11]. On rencontre, par exemple, des générateurs d'oscillations à grille et plaque accordées, autobloqueurs à quartz, hétérodynes à battements. Quant aux cellules de titrages, de formes et de dimensions très variables, ce sont des dispositifs à condensateur ou à self.

Nous avons seulement l'intention de vous présenter un appareil simple, utilisable même pour un contrôle en atelier, et les résultats qu'il a permis d'obtenir surtout pour le dosage de bases organiques de constitution très variée.

Cet appareil a pu être réalisé grâce à la collaboration technique de Monsieur BRUAS, à qui il nous est agréable d'adresser nos vifs remerciements.

APPAREIL (*cf.* Fig. 1)

A. L'oscillateur

Nous avons choisi un système d'oscillations entretenues et stabilisées à 2 Mc par quartz piézoélectrique inséré sur le circuit grille d'une lampe oscillatrice 6 AQ 5.

La cellule de dosage est disposée en parallèle de l'ensemble self capacité du circuit plaque. Nous reviendrons plus loin sur la forme de cette cellule.

La tension grille de la lampe oscillatrice est appliquée à un potentiomètre qui permet d'en prélever une fraction convenable dont on mesure les variations par un voltmètre à lampe.

B. L'appareil de mesure

C'est essentiellement un voltmètre électronique utilisé en appareil de zéro. Il comprend un tube amplificateur 6 AU 6 à tension cathodique compensée et un tube cathodique indicateur de zéro. La tension plaque du tube amplificateur est appliquée directement à la grille du tube cathodique.

C. L'alimentation haute tension

L'alimentation est réalisée à partir du réseau 120 V régulé par transformateur à fer saturé; elle est redressée, filtrée et régulée de nouveau par tube au néon.

D. La cellule de dosage

Son rôle est déterminant dans le succès de la technique de dosage H.F.

Ses dimensions, sa forme, la disposition des électrodes ont une grande importance. Nous sommes encore en train d'en étudier les caractéristiques.

Les quelques résultats dont nous allons vous entretenir ont été obtenus principalement avec une cellule du type de la Fig. 2, qui est d'un emploi très pratique pour le manipulateur, mais qui manque un peu de sensibilité.

Cette cellule peut être équipée avantageusement d'un couvercle rodé laissant un passage à l'agitateur et à la pointe de la burette qui contient le réactif.

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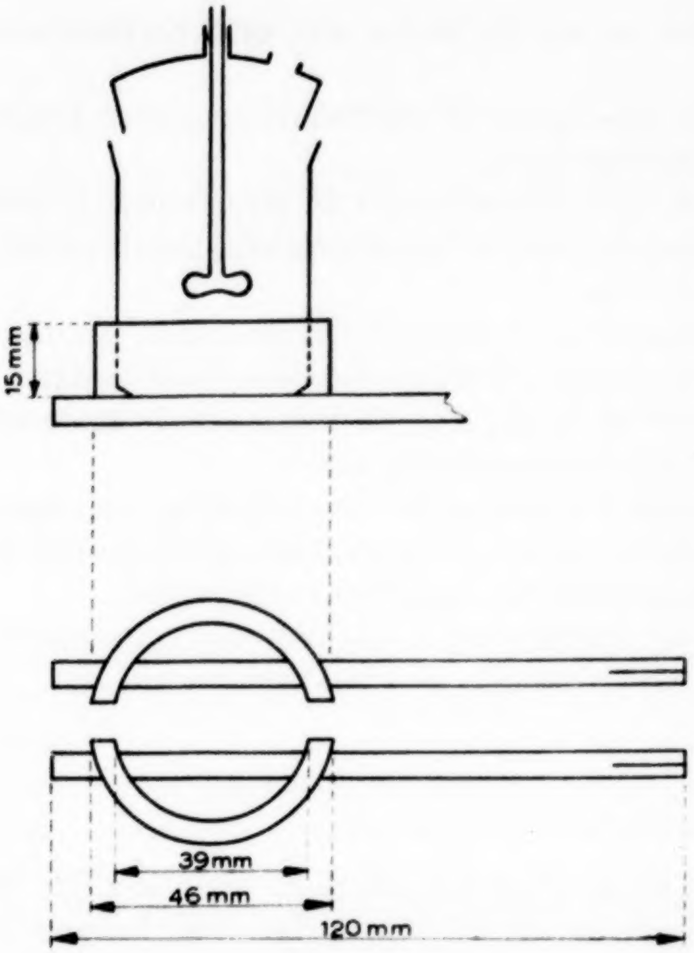
15mm
39mm
46mm
120mm

Fig. 2.

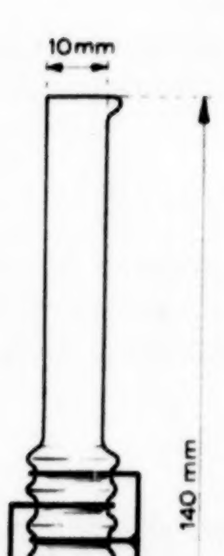
10mm
140mm
16mm

Fig. 3.

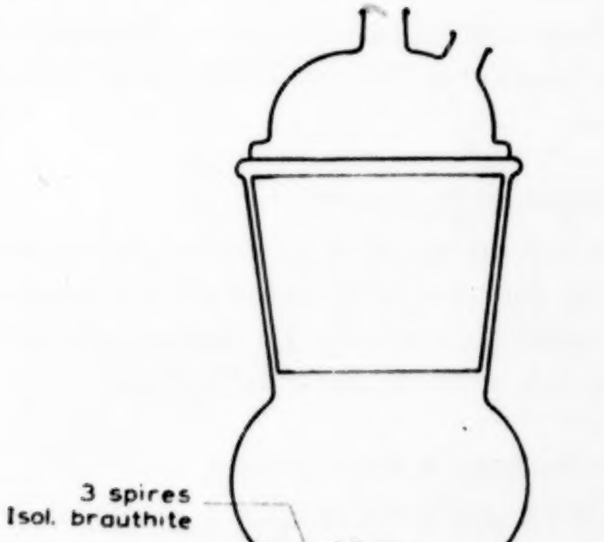
3 spires
Isol. brauthite
38mm
40mm
45mm
23mm

Fig. 4.

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En utilisant, au lieu de la cellule du type de la Fig. 2, soit l'un, soit l'autre des deux types représentés (Fig. 3 et Fig. 4), on peut facilement multiplier la sensibilité par 3 ou 4. La cellule du type représenté par la Fig. 3 est utilisable avec n'importe quel genre de solvant.

E. Emploi de l'appareil

Il peut être utilisé, soit à la résonance: méthode dite par „conductance", soit au maximum de la pente de la courbe de résonance, au voisinage du point de décrochage: méthode dite par „capacitance".

Les deux modes opératoires donnent très sensiblement les mêmes résultats quand on opère en milieu acétique, mais la mesure en capacitance est plus sensible quand on opère dans d'autres solvants et toujours beaucoup plus rapide.

APPLICATIONS

Pour le moment, les principales applications de ce montage ont été limitées au titrage de bases organiques diverses en milieu acétique. Nous avons toutefois réalisé aussi des dosages d'acides organiques ou de phénols à l'aide des cellules représentées par les Figs. 3 et 4.

A. Conditions du dosage

(a) Humidité. Il est important pour effectuer ces dosages que le solvant du produit à doser, ainsi que la solution de titrage, aient une teneur en eau aussi faible que possible. S'il n'en est pas ainsi, on constate non seulement une diminution de la netteté du point d'équivalence mais encore, dans certains cas, un déplacement de celui-ci (Fig. 5).

La Fig. 5 représente les courbes de titrage de caféine anhydre avec des teneurs en eau des réactifs de 0.06%, 0.53% et 1.06% en p/v obtenues avec la cellule représentée Fig. 2. Pour 1% d'eau, le point d'équivalence est à peine marqué et le titre mesuré n'est plus que de 80% du titre attendu. Nous n'avons pas encore trouvé d'explication valable à cette dernière constatation.

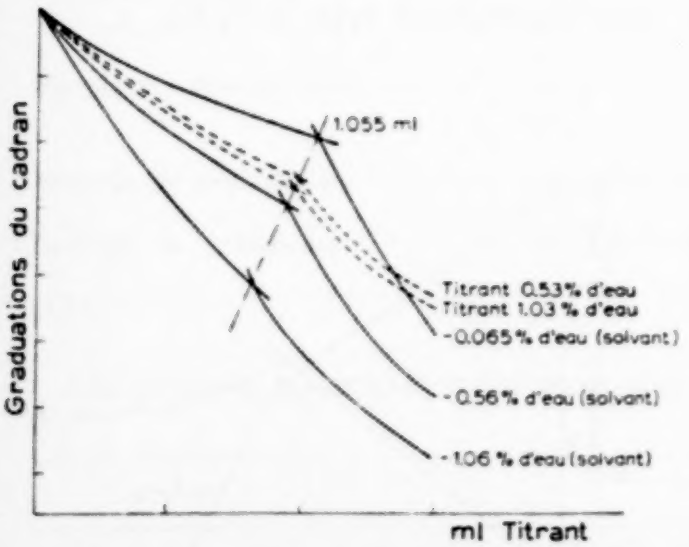

Fig. 5. Influence de l'eau dans le titrage de caféine par haute fréquence.

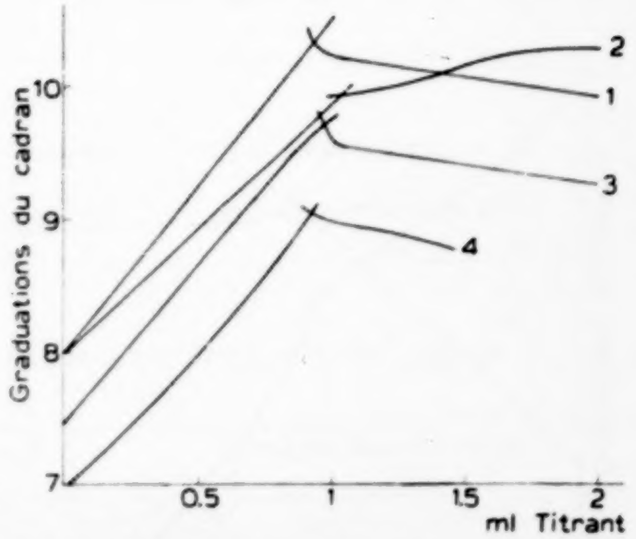

Fig. 6. Dosages en retour. 1. Potassium acétate, 2. Méthane sulfonate de Lomidine, 3. Potassium laurate, 4. Potassium phtalate acide.

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(b) Quantité de solvant. Prise d'essai. Solution de titrage. La cellule de la Fig. 2 est prévue pour une capacité limite compte tenu de l'agitation de 40 ml.

La quantité minimum de solvant à mettre en oeuvre avant l'addition de la liqueur titrée est comprise entre 10 et 15 ml, les quantités de matière à doser étant de l'ordre de 0.1 à 0.3 milliéquivalents avec une solution de titrage 0.1*N*.

(c) Température. Des variations de température de quelques degrés dans la cellule sont sans effet sur le résultat du dosage. Toutefois, la netteté est plus grande au voisinage de 20°. Pour l'utilisation courante, il ne paraît pas nécessaire de thermostater.

B. Titrages directs et titrages en retour

Chaque fois qu'il y a précipitation au cours du titrage, on constate des perturbations diminuant la précision des lectures. Cette constatation avait déjà été faite par LANE[6].

Par contre, une fois la précipitation terminée, ces perturbations ne se produisent pas. Il en résulte que, chaque fois qu'une précipitation est succeptible de se produire, on doit opérer en retour.

ex.: Sels de potassium
Pentamidine (Lomidine) (Fig. 6) } par l'acide perchlorique.

Même lorsqu'il ne se produit pas de précipitation, on a quelquefois intérêt à opérer en retour.

ex.: Bétaïne base (Fig. 7)
Diphénylguanidine (Fig. 8)
Théophylline (Fig. 9) } par l'acide perchlorique.

Résultats de dosages. En dehors de l'acétate de sodium, du phtalate acide de potassium et du salicylate de sodium qui ont servi à l'étalonnage des solutions d'acide perchlorique, les produits suivants ont été dosés avec la cellule du type de la Fig. 2.

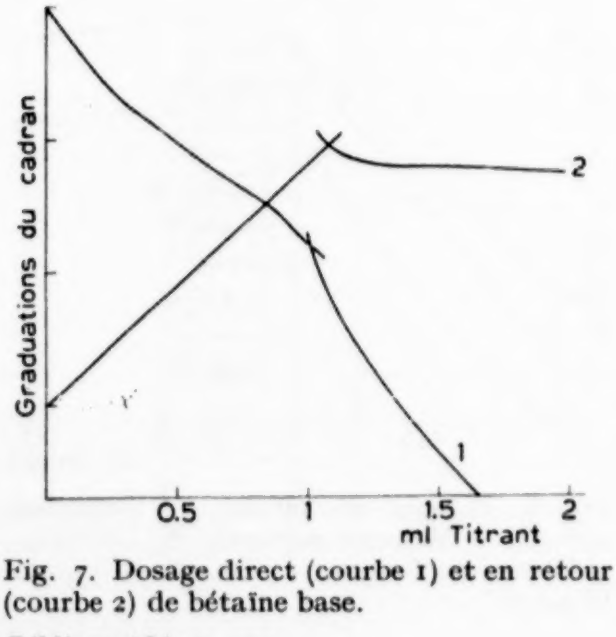

Fig. 7. Dosage direct (courbe 1) et en retour (courbe 2) de bétaïne base.

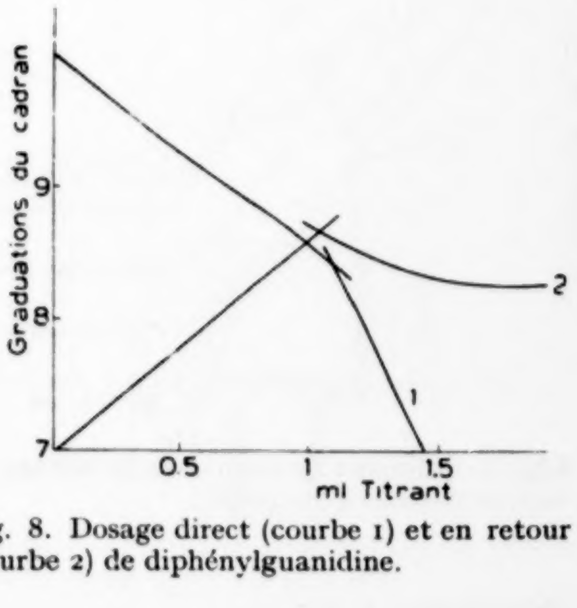

Fig. 8. Dosage direct (courbe 1) et en retour (courbe 2) de diphénylguanidine.

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TABLEAU I

Produit	*Titre obtenu par H. F.* (%)	*Titre par une autre méthode* (%)
Diphénylguanidine	97.5 } titrage 98.3 } direct 98.5 en retour	98.8 (indicateur)
Glycocolle	98.0 99.0	99.2 (potentiométrie)
Bétaïne base	97.3 } titrage 97.3 } direct 97.1 en retour	97.0 (indicateurs)
Bétaïne citrate	98.8 99.5	99.5 (potentiométrie)
Choline citrate	100.0 100.6	100.1 (potentiométrie)
Caféine anhydre	100.0 99.5	—
Théophylline cristallisée (à une molécule d'eau)	99.0 } titrage 100.0 } direct 99.8 en retour	100.0 (argentimétrie)
Sulfanilamide	100.2 100.2	99.5 (potentiométrie)
Sulfaguanidine	99.6 99.6	—
Sulfacétamide sodé	99.4 99.4	99.6 (alcalimétrie)
Méthane sulfonate de Pentamidine (Lomidine)	98.1 (titrage en retour)	98.5 (au tétraphénylbore)
Péthidine (Dolosal)	101.1 100	100.5 (potentiométrie)
Mescaline chlorhydrate	98.5 99.2	99.0 (potentiométrie)
Acétate de potassium	94.5 (titrage en retour)	95.0 (indicateur)
Laurate de potassium	99.5 (titrage en retour)	99.8 (potentiométrie)

Les produits suivants ont été dosés avec la cellule du type représenté Fig. 4:

Produit	*Titre obtenu par H. F.* (%)	*Titre par une autre méthode* (%)
Acide benzoïque*	100	100
Acide salicylique*	100	100

* Milieu: méthanol + benzène (2 + 8); liqueur titrante: méthylate de sodium $0.1N$.

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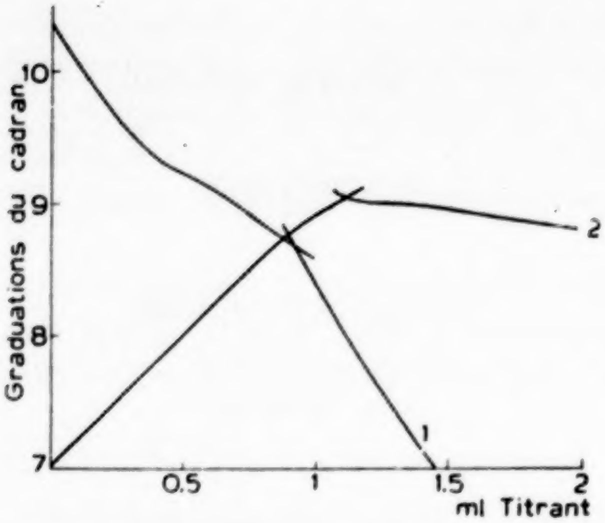

Fig. 9. Dosage direct (courbe 1) et en retour (courbe 2) de théophylline Codex.

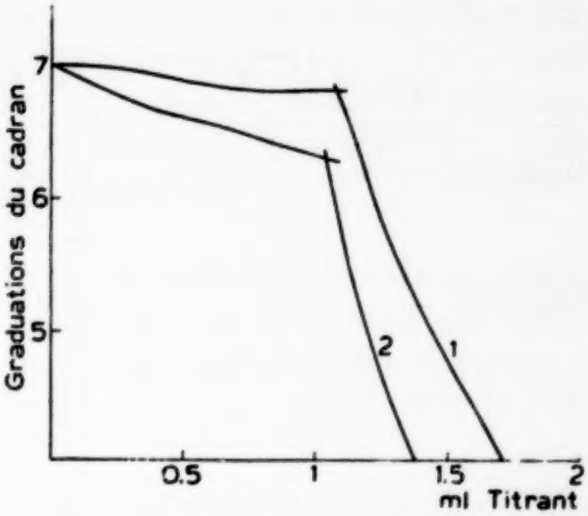

Fig. 10. Dosage de Péthidine (Dolosal) (courbe 1) et mescaline chlorhydrate (courbe 2).

POSSIBILITÉS ET PRÉCISION DE LA MÉTHODE

A. Possibilités

(a) Le dosage n'est possible que pour les produits initialement solubles dans le milieu.

Par exemple: la théobromine,
le tartrate acide de potassium,
le sulfate de streptomycine,

insolubles ou très difficilement solubles dans l'acide acétique, n'ont pu être titrés dans ce milieu.

(b) Les produits dosables par potentiométrie le sont aussi par haute fréquence.

En ce qui concerne les sels d'acide fort en milieu acétique:

Les chlorhydrates se titrent en complexant *in situ* HCl par l'acétate mercurique selon la méthode de Pifer et Wollish. C'est ainsi qu'ont été dosés Péthidine (Dolosal) et chlorhydrate de mescaline (Fig. 10).

Les sulfates ne donnent pas de bons résultats.

Le titrage du méthane sulfonate de Lomidine a donné un résultat convenable alors que la potentiométrie est impossible dans ce cas particulier.

(c) Le titrage des bases très faibles, comme la caféine, la théophylline, la sulfaguanidine, très difficile par potentiométrie, a pu être effectuée avec une bonne précision par H.F.

D'autre part, la facilité de manipulation de la cellule en a rendu l'emploi possible en atelier pour le contrôle rapide de la teneur en anhydride acétique de mélanges complexes. On fait dans ce cas l'acétanilide et l'on titre l'excès d'aniline en retour par l'acide perchlorique.

B. Précision

Le point d'équivalence s'évalue à ± 0.01 ml de solution $0.1N$, ce qui correspond à une précision relative de ± 1%, valeur qui est du même ordre que celle que l'on peut déduire des tableaux de résultats de diverses publications[6,7].

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CONCLUSION

Nous avons réalisé un montage relativement simple, pratique et économique, qui a permis de titrer aisément à 1% près un certain nombre de bases organiques très diverses en milieu acétique avec des prises d'essai à l'échelle de la semi microanalyse.

Nous avons pu doser ainsi certains produits qu'il est impossible de doser par d'autres méthodes.

Nous sommes en train de terminer la mise au point de quelques modèles de cellules de titrage qui nous ont d'ores et déjà permis d'augmenter largement la sensibilité et avec lesquels il devient possible d'effectuer une plus grande variété de dosages dans d'autres milieux non aqueux.

RÉSUMÉ

Un appareil simple est décrit; la fréquence d'oscillation est stabilisée par un quartz piezoélectrique (fréquence fondamentale = 2 Mc). Les variations de tension grille de l'oscillateur sont amplifiées et compensées, le réglage étant effectué à l'aide d'un indicateur cathodique. La mesure peut être faite soit en conductance, soit en capacitance.

Trois modèles de cellules de titrage sont présentés. On indique quelques exemples de dosage et les conditions dans lesquelles ils doivent être effectués.

SUMMARY

A simple apparatus is described; the oscillation frequency is stabilized by a piezoelectric quartz crystal (fundamental frequency = 2 Mc). The variations of the grid tension of the oscillator are amplified and compensated, regulation being effected by means of a cathode ray indicator. The determinations can be made by using either changes in conductance or changes in capacitance.

Three models of titration cells are presented. The author gives several examples of determinations and the conditions in which they should be carried out.

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DISCUSSION

Dr. Mechelynck (Mol, Belgique):

La caféine peut être dosée par une autre méthode: son pouvoir suppresseur de maximum polarographique, notamment dans le cas de l'uranium. Je pense que cette méthode ne peut être négligée.

Ir. Dr. Y. Conseiller:

Méthode un peu spéciale et probablement beaucoup moins rapide.

Mr. A. Berlin (Seattle, U.S.A.):

Dans le cas où le titrage conductimétrique est possible y a-t-il un avantage à utiliser la méthode de dosage à haute fréquence?

Ir. Dr. Y. Conseiller:

Oui, pour la rapidité et la faible quantité de produit mise en oeuvre.

NEWER METHODS OF DETERMINING ELECTROLYTIC CONDUCTIVITY

by

V. S. GRIFFITHS

Battersea College of Technology, London (England)

The use of conventional dipping electrode systems in the determination of electrolytic conductivities is associated with a number of experimental difficulties, many of which are directly associated with the electrodes themselves and which are classified under the term "polarisation". With concentrated electrolyte solutions, especially where the contact time is long, corrosion problems are also encountered. Many attempts have been made to eliminate the use of immersed electrodes, mostly using high frequency alternating current[1-28]. The work described here makes use of a "non-contacting electrode system" in conjunction with a three-terminal transformer ratio-arm bridge operating at audiofrequencies[29-32]. The conventional bridges used can be regarded as two terminal bridges. These are capable of high sensitivity but often possess poor stability, and to obtain a high degree of accuracy it is necessary to use a Wagner earth arrangement if a wide range of measurements is to be carried out, due to effect of stray impedances and capacitance. The use of a three-terminal transformer bridge offers considerable advantages in this respect. The basic circuit of a three-terminal network is shown in Fig. 1, where the impedance to be measured is Z_u, but the effects of stray impedances Z_{en} and Z_{in} must be removed. Fig. 2 shows the network applied to the bridge where Z_{en} shunts a voltage transformer and Z_{in} shunts a current transformer. It is convenient to refer to E as the voltage terminal, to I as the current terminal and to N as the neutral. Assuming ideal transformers, Z_s, the standard impedance is adjusted to give zero voltage at the detector when there must then be zero core flux in the current transformer and

$$N_1 \cdot I_u = N_2 \cdot I_s \qquad (1)$$

where N_1 is the number of turns on the windings connected to the unknown, N_2 the number of turns connected to the standard, whilst I_u and I_s are the currents in the

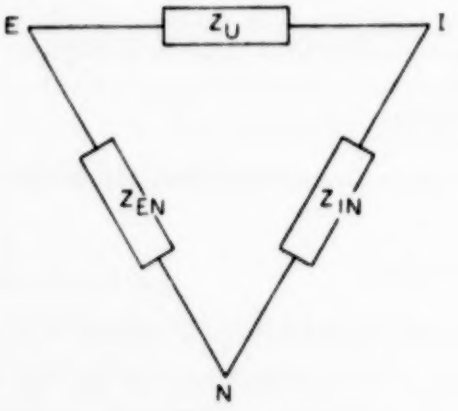

Fig. 1.

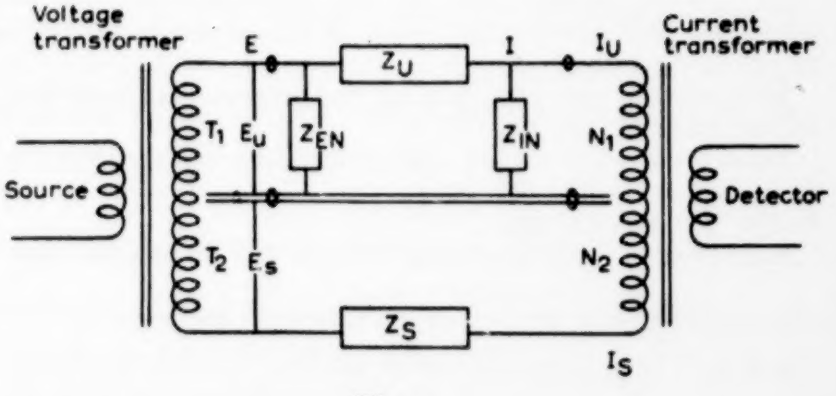

Fig. 2.

unknown and standard, respectively. Under the condition of zero core-flux there is zero voltage across the windings of the current transformer. The connections to both Z_u and Z_s on the current transformer side are thus at neutral potential. The voltage across Z_u is E_u and across Z_s is E_s, when

$$I_u = E_u/Z_u \qquad (2)$$

$$I_s = E_s/Z_s \qquad (3)$$

and thus from eqn. (1)

$$N_1E_u/Z_u = N_2E_s/Z_s \qquad (4)$$

But the voltage ratio, E_u/E_s, equals the turns ratio, T_1/T_2, so that at balance the equation becomes:

$$Z_u = N_1/N_2 \cdot T_1/T_2 \cdot Z_s \qquad (5)$$

Thus, if the transformers are ideal, neither Z_{en} nor Z_{in} cause any errors. At balance Z_{in} has no voltage across it and therefore draws no current. Its effect is to reduce the off-balance sensitivity by lowering the detector input impedance, and this can be overcome by increasing the gain. The impedance Z_{en} loads the source, and by drawing current through the source impedance reduces the applied voltage E_u. The measurement, however, does not depend on absolute voltage but on the ratio E_u/E_s. In an ideal transformer this is a constant equal to the turns ratio, and a shunt on one winding reduces the voltages on all windings by the same proportions. In practice, whilst the transformers cannot be regarded as ideal and shunt impedances will produce small errors, careful construction can reduce the errors to negligible proportions, and in any case the effects of shunt loading can be compensated.

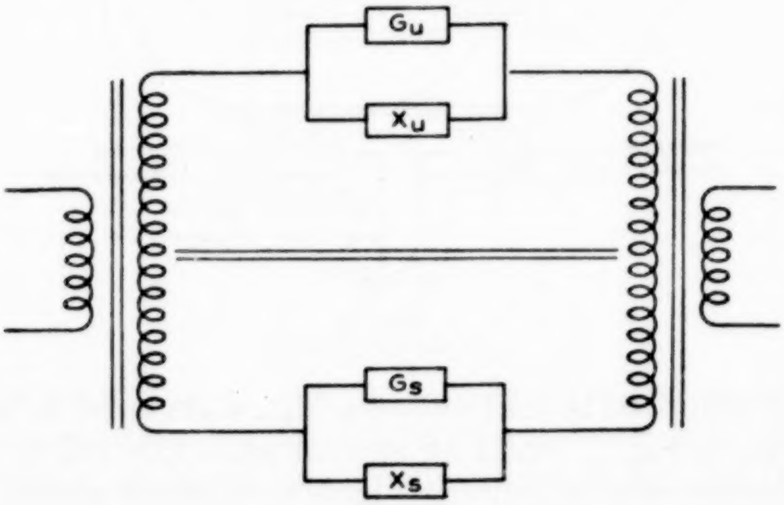

Fig. 3.

Equation (5) can be rewritten in terms of conductances

$$G_u = (G_s\,T_2) \cdot N_2/T_1N_1 \qquad (6)$$

Let (G_sT_2) represent the standard, then it will be seen that it is immaterial whether the number of turns be fixed and the conductance varied, or the conductance fixed and the number of turns varied. Using the latter the number of standards can easily be reduced to one per decade. In practice the unknown is often a complex impedance, and Fig. 3 shows the bridge such that the standard and unknown impedance have been divided into resistive and reactive components and similar arguments can be advanced for the determination of the reactive component. The measurements are dependent on the product of two turns-ratios and since each of these can easily be 1000:1, the overall ratio is a million to one. Further measurement of impedances remote from the bridge presents no great problem since the capacitance of long connecting leads and spurious impedances connected to the measuring terminals are counteracted by the use of the third terminal.

The frequency of the oscillator is of importance only in fixing the size of the probe unit, and most of the measurements described were made at 1000 c/s, although a few measurements have been made at higher frequencies (1592 c/s and 10,000 c/s). The detector consists of a tuned amplifier linked to the current transformer, the balance point being detected with an oscilloscope or integral magic eye.

Whilst the bridge can be used with conventional electrodes it also permits the determination of conductivity with non-contacting electrodes. Consider the case where T_1 and N_1 are made single turns, so that the balance equation becomes

$$G_u = N_2 \cdot T_2 \cdot G_s \quad \ldots \ldots \ldots \ldots \quad (7)$$

The physical nature of the windings is unimportant and there is no reason why the cores of the voltage and current transformers, which in practice are wound on high permeability Mumetal toroidal cores, should not be linked by a closed annulus of conducting liquid contained in an insulating, *e.g.*, glass tube. A method of bringing this about is shown in Fig. 4, where an annular glass loop cell is used, although for many purposes similar cells of polythene have been found useful. The transformers are moulded into an insulating material, and where the electrolyte is inert with respect to the moulding, the probe may be immersed directly in the test-solution, provided the container is large in comparison to the probe. The size of the probe is a function of the frequency used, the one shown being operated at 1000 c/s, and the higher the oscillator frequency used the smaller the probe becomes.

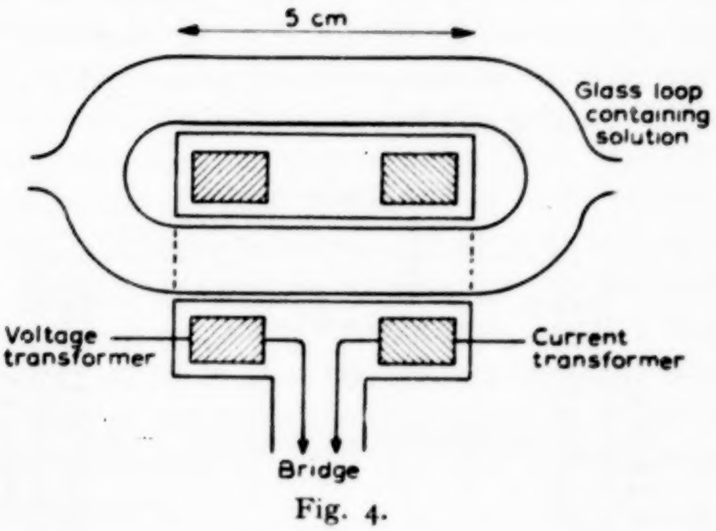

Fig. 4.

These types of units have been used to determine the conductivity of a variety of solutions, being especially suited to concentrated solutions.

The facility with which the bridge measures the capacitance term as well as the conductance term has made it useful for the determination of impurities, *e.g.* water in organic liquids.

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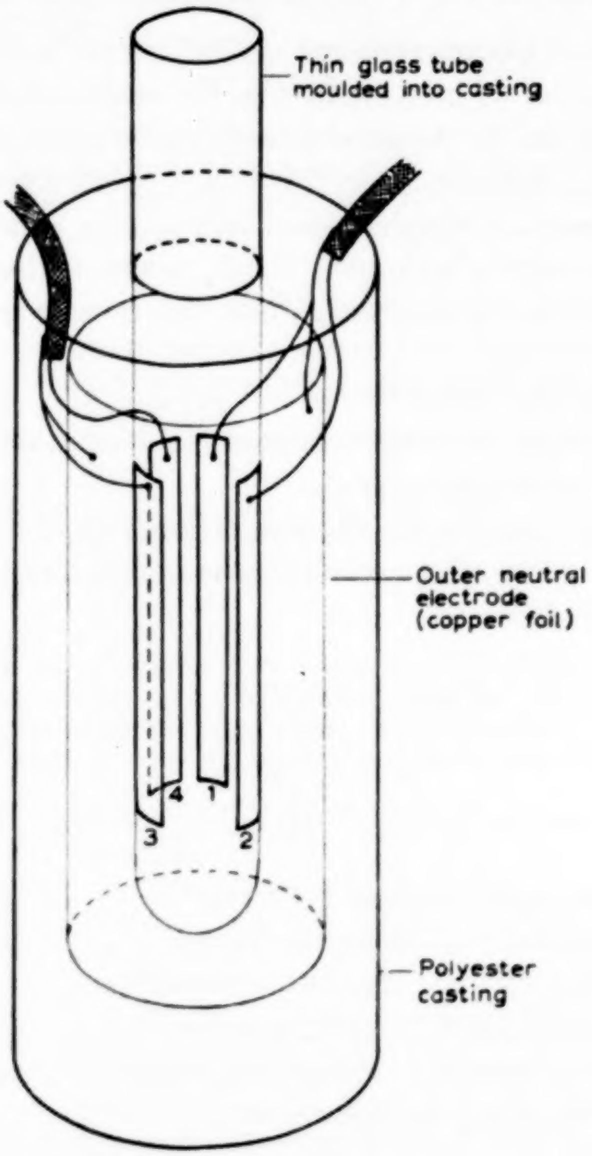
For this purpose the "capacity cell" shown in Fig. 5 was used.


Thin glass tube moulded into casting
Outer neutral electrode (copper foil)
4
1
3
2
Polyester casting

1 and 3 = Inner neutral electrodes
2 = Voltage electrode
4 = Current electrode

Fig. 5.

EXPERIMENTAL

The conductivities were determined at 25° ± 0.02 in cells whose cell constants were used using the "demal solutions" of JONES AND BRADSHAW[33]. The "capacity-cell", by virtue of its construction, has a capacity term involving the glass of the tube as dielectric, and this was corrected tor by determination of this capacity by filling the cell with mercury. Otherwise, conventional methods were adopted with regard to solvent purity, etc.

RESULTS AND DISCUSSION

(*1*) *Conductivity measurements using loop cells or probe*

The determination of the conductivity of concentrated electrolyte solutions has been described elsewhere[29,32], and where results are available in the literature there are found to be no real differences from those obtained using conventional electrode systems. The corrosive fluids are concerned, whilst the conductivities of flowing liquids or liquids advantage lies in the fact that electrode problems do not arise, particularly where in vats can easily be determined with the robust probe and with little restriction of cable length.

Conductivity titrations likewise present similar curves to those obtained with conventional systems. A point of interest here is the result obtained with concentrated sulphuric acid. A minimum in the conductance curve exists at approximately 100% acid, and a conductivity determined in this region could represent concentrations on either side of the minimum. A simple way of determining which concentration existed was to dose the system with a little 98% H_2SO_4, when, if the acid concentration was below 100%, the conductivity increased whilst the reverse held on the other side.

(2) *Measurements using the "capacity cell"*

A series of measurements on "water-contaminated", 1:4-dioxan are shown in Table I, where the frequency used was 1592 c/s.

The calculations were based upon the conversion formulae shown below where the parallel readings made with the bridge were converted to series readings, due allowance being made for the glass dielectric.

$$C_{m.s.} = C_{m.p.} + \frac{G^2_{m.p.}}{\omega^2 C_{m.p.}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

$$\frac{1}{C_{c.s.}} = \frac{1}{C_{m.s.}} - \frac{1}{C_g} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

where C_g = capacity of glass dielectric
$C_{m.s.}$ = capacity of "measured series"
$C_{m.p.}$ = capacity of "measured parallel"
$C_{c.s.}$ = capacity of "corrected series"
$G_{m.p.}$ = conductivity "measured parallel"
ω = frequency in radians/sec.

Up to 5% water the results agree well with those of ÅKERLÖF AND SHORT[34], but above this concentration the dielectric constant value obtained is meaningless, owing to the effect of the conductivity. This method has allowed the determination of relatively small amounts of water (0.1% ± 33%) in organic liquids which have, when pure, low dielectric constants. Indeed, good results have been obtained for water-contaminated acetone (E 21) and it has been possible to estimate acetone in synthetic cyclohexane-acetone mixtures, although with much less accuracy. For many purposes, where the conductivity term is negligible it has been possible to obtain results from a plot of the parallel capacity against concentration of polar contaminant.

TABLE I

%age water	*C measured (μμF)*		*C corrected*	*G measured (μmho)*	*D*
	Series	*Parallel*			
0	—	0.420	0.4307	0	2.10
1	—	0.476	0.4897	0	2.38
2	—	0.506	0.5218	0	2.54
3	0.588	0.587	0.6090	0.0002	2.96
4	0.653	0.640	0.6794	0.0009	3·30
5	0.698	0.664	0.7278	0.0015	3·54
7	5·089	0.989	7·2730	0.2014	(35)
Mercury	—	16.96		0.003	

ACKNOWLEDGEMENTS

The author wishes to thank the Wayne-Kerr Laboratories, and in particular, Mr. R. Calvert, who designed and built the bridges.

SUMMARY

This paper describes, in outline, the theory, construction and use of a three-terminal transformer ratio-arm bridge. The effect of strong impedance and capacitance are minimized without the use of a Wagner earth. By using special cells the use of contacting metal electrodes can be eliminated. The use of the bridge for measuring dielectric constants is also described.

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DISCUSSION

Dr. G. C. Barker (Harwell):

I should like to know what accuracy is attainable using the conductance probe.

Dr. V. S. Griffiths:

In concentrated solutions not much better than 0.5% at 1000 c/s, but at 50 kc/s better than 0.1%.

NEUE THEORIE DER ELEKTROLYSE UND DER REDOXYDATIONEN*

von

A. SCHLEICHER†

Aachen (Deutschland)

Durch meine Untersuchungen über die sog. innere Elektrolyse und durch den Vergleich dieser mit der bekannten äusseren Elektrolyse bin ich zu einer neuen Theorie der Elektrolyse als solcher wie auch der rein chemischen Redoxydationen gelangt, welche ich Ihnen heute kurz mitteilen möchte.

Das Gemeinsame der beiden Elektrolysen ist die Verwendung zweier Metallelektroden und damit das Auftreten eines anodischen und eines kathodischen Vorgangs; ihre Unterschiede bestehen vor allen Dingen darin, dass bei der inneren Elektrolyse zwei Elektrolyte gebraucht werden, während sich bei der äusseren Elektrolyse beide Elektrodenvorgänge in einem gemeinsamen Elektrolyt abspielen. Das macht sich bei der ersteren in der praktischen Anwendung vorteilhaft bemerkbar und bedingt bei der letzteren eine gewisse gegenseitige Abhängigkeit im Ionenverlauf.

Die Induktion

Man wird dies leichter verstehen, wenn man sich für die Vorgänge an den Elektroden des Induktionsbegriffes bedient.

Unter einer Induktion sind hier die Erscheinungen zu verstehen, welche beim Einwirken eines Elektronenstromes auf einen metallischen Leiter eintreten und welche sich dann auch auf einen Elektrolyt übertragen lassen. Es erscheint in beiden Fällen infolge des mit dem Elektronenfluss verbundenen magnetischen Feldes eine neue, sog. induzierte Spannung, eine Spannungsüberlagerung, also Spannungssteigerung, und es findet eine Bewegung des oder der Ladungsträger statt. Legt man also an eine in einem Elektrolyt befindliche Metallelektrode einen elektrischen Strom an, so werden die Anionen in Richtung auf die Gegenelektrode gedrängt, während sich die Kationen in Richtung auf die erstere zu bewegen. Beim Erreichen der jeweiligen Gegenelektrode vollzieht sich an ihnen, als der Anode und der Kathode, infolge der Entladung die Bildung induzierter Spannungen, deren Grösse durch die Elektrodenpotentiale gegeben ist. Die Stärke der Bewegung kommt in den bekannten Wanderungsgeschwindigkeiten zum Ausdruck. Je nachdem nun, ob die Ionenwanderung in einem gemeinsamen oder in getrennten Elektrolyten erfolgt, kann man zwei verschiedene Arten von Induktionen unterscheiden; sind beide Elektrolyte von einander getrennt, so handelt es sich um eine einseitige oder Selbstinduktion, sind aber beide in einem Raum vereinigt, so liegt eine gegenseitige Induktion vor. Fliessen beide Ströme im gleichen Raume, aber in entgegengesetzter Richtung, findet also eine gegenseitige Durchdringung der wandernden Ionenfelder statt, so unterliegen sie einer gegenseitigen Induktion im Sinne der Physik elektrischer Ströme. Daraus folgt, dass die *innere Elektrolyse auf Selbstinduktion, die äussere aber auf gegenseitiger beruht.*

---

* Der Inhalt des obigen Vortragtextes wird etwas ausführlicher erscheinen als X. Fortsetzung der Artikelreihe des Verfassers, *Katalyse und Induktion*, in der *Z. anal. Chem.*

Die Magnetfelder

Inwieweit bei den beiden Arten von Elektrolysen Magnetfelder auftreten, ist noch wenig studiert worden. Aus den Beobachtungen an elektrischen Strömen in Metallteilen und -drähten ist aber bekannt, dass beim Einschalten eines Stromes Energie für das entstehende Magnetfeld verbraucht wird, so dass der Strom nicht sofort in voller Stärke fliesst. Die aufgespeicherte Energie steht zum Abbau des Feldes wieder zur Verfügung. Man spricht von einer *Trägheit* des Feldes wie auch von der Trägheit der Masse. Schaltet man aber die Teile eines Geräts der inneren Elektrolyse zum Kurzschluss zusammen, so kann man beobachten, dass die Stromstärke nur langsam ihren Höchstwert erreicht, um dann wieder bis nahe zum Nullwert abzusinken. Somit *besteht die innere Elektrolyse in dem Aufbau und Abbau eines Magnetfeldes.*

Die Redoxydationen

Bei allen elektrolytischen Vorgängen vollziehen sich Reduktionen und Oxydationen, gleichgültig, ob es sich um äussere oder innere Elektrolysen handelt. Es ist also zu vermuten, dass sich Induktionen beider Art auch bei jenen feststellen lassen, denn auch bei ihnen bewegen sich Elektronen, sie wandern vom Reduktans zum Oxydans, während sich die gleiche Zahl positiver Ladungseinheiten in umgekehrter Richtung verlagert. Es entstehen neue, induzierte Spannungen, die sich an unangreifbaren Elektroden als Redox-Potentiale messen lassen. Es finden also *gegenseitige Induktionen* statt.

Man kann aber auch *Selbstinduktionen* beobachten, wie dies an dem bekannten Vorgang der Eisenoxydation durch Permanganat in salzsaurer Lösung als Beispiel gezeigt werden soll. Sie vollzieht sich bekanntlich nur bei Gegenwart eines beträchtlichen Zusatzes von Mangan(II)-Ionen reibungslos. Im anderen Falle entsteht nach der gebräuchlichen Darstellung durch „Induktion" eine Chlorgas-Entwicklung. Dabei soll, wie man annimmt, ein durch Übersteigerung der Wertigkeit des Eisenions gebildetes Ferrylion schliesslich die Eisenoxydation herbeiführen, und es soll sein Oxydationspotential durch Zusatz von Mn(II)-Ionen soweit vermindert werden, dass die Chlorgas-Entwicklung ausbleibt.

Jede einseitige Wertigkeitssteigerung ist aber bereits eine Selbstinduktion und aus der Tatsache, dass es ein Mangel an Mangan-Ionen ist, der den glatten Verlauf verhindert, folgt, dass dieses Ion ein wesentlicher Bestandteil der chemischen Umsetzung ist. Es sollte somit auch in ihre stöchiometrische Gleichung mit einbezogen werden.

Wird nun Mn(II)-Ion durch Selbstinduktion zu Mn(III)-Ion gehoben, fällt es aber alsbald wieder zu Mn(II)-Ion ab, weil ersteres in der salzsauren Lösung nicht beständig ist, so liegt hier ein katalytischer Vorgang vor, durch den die Selbstinduktion in eine gegenseitige übergeführt wird. Man könnte dann die folgende gekürzte Bruttogleichung für den schnellen Verlauf aufstellen:

$$Mn^{+7} + 5\,Mn^{+2} + 5\,Fe^{+2} = 6\,Mn^{+2} + 5\,Fe^{+3}.$$

Hier werden je 1 Mn^{+7} von den Eisen- und Manganionen 5 Elektronen ausgesandt; sie hinterlassen Fe^{+3}- und Mn^{+3}-Ionen. Die ersteren sind beständig, die letzteren aber nicht, sie werden in der salzsauren Lösung wieder zu Mn^{+2}-Ionen aufgeladen. Die vom Eisen freigegebenen 5 Elektronen laden das Mn^{+7}-Ion zu Mn^{+2}-Ion auf. Es wird also neues Mn(II)-Ion gebildet, wie der Zuwachs an ihm auf der rechten Seite der Gleichung zeigt. Dadurch bekommt der ganze Vorgang den Anschein eines autokatalytischen.

Die Gleichung lehrt ferner, dass die Menge an zusätzlichen Mangan(II)-Ionen derjenigen des zu bestimmenden Fe(II)-Ions zumindest äquivalent sein muss. Dies trifft auch nach der für die Titration bestehenden Vorschrift in etwa zu.

Die Hemmung des Vorgangs liegt nach allgemeiner Auffassung am Permanganatkomplex, das Mn^{+7}-Ion liegt nicht frei vor, sondern ist durch Sauerstoff-Ionen gebunden. Der dadurch bedingte „innere" Widerstand kann aber nur durch ein elektrisches oder magnetisches Moment behoben werden. Ein solches ist durch das Auf und Ab des katalytischen Vorgangs gegeben, indem der Elektronenfluss eine Stromschleife bildet und dadurch ein Magnetfeld erzeugt, welches seinerseits den Elektronenfluss begünstigt. Die freiwerdenden Sauerstoff-Ionen werden durch die reichlich vorhandenen Protonen gebunden.

Am Ende des ganzen Vorgangs ist eine vollständige Entspannung eingetreten; es hat eine *gegenseitige* und *gleichzeitige Aufwertung* der *niederen* und eine *Abwertung* der *höchsten Ladungsträger* stattgefunden.

ZUSAMMENFASSUNG

Es wird gezeigt, daß die Induktion elektrischer Ströme ein *tertium comparationis* zwischen der äusseren und der inneren Elektrolyse ist, indem die erstere auf gegenseitiger, die letztere auf Selbstinduktion beruht. Daraus ergibt sich eine neue Theorie der Elektrolyse. Das Gleiche gilt auch für elektrodenfreie Redoxydationen. Auch hier können beide Arten der Induktion erkannt werden.

SUMMARY

It has been pointed out that the induction of electric currents is a *tertium comparationis* between the external and the internal electrolysis, the former depending on mutual induction and the latter on self-induction. This has given rise to a new theory of electrolysis. The same applies to electrode-less redox reactions, in which both types of induction can also be found.

End of the papers presented at the
Symposium on Modern Electrochemical Methods of Analysis

BOOK REVIEWS

L'Analyse Qualitative et Réactions en solution, par G. CHARLOT, Masson et Cie, Paris, 1957, 368 p.

Une nouvelle édition du livre d'analyse qualitative du Professeur CHARLOT vient de sortir de presse. Elle a été entièrement refondue et la nouvelle présentation en est extrêmement soignée. On y trouve les plus récentes applications de la physicochimie à l'analyse, ce qui a permis de simplifier considérablement l'identification des ions. En jouant sur le pH, les potentiels d'oxydoréduction, les complexes et leur stabilité, la solubilité, on parvient à rendre plus sélectif les réactifs et on évite ainsi un grand nombre de séparations. ,,La chimie analytique raisonnée", tel pourrait être le titre de cet ouvrage, remarquable instrument pour l'étudiant comme pour le chimiste chevronné.

La première partie de ce livre comprend, sous le titre de généralités, l'étude de la constitution de l'atome, de la coordinence et des équilibres chimiques. Puis l'auteur examine les équilibres homogènes et les réactions en présence de deux phases: précipitation, extraction, échangeurs d'ions, etc. et enfin l'étude des cas où l'équilibre n'est pas atteint: réactions lentes, catalyse, indicateur et réactifs, relations entre propriétés et structure terminent ces considérations théoriques.

La seconde partie traite de l'analyse qualitative. Chaque ion y est décrit avec ses propriétés essentielles, les diverses constantes qui s'y rapportent en sont données dans des tableaux forts complets. On y trouve aussi les réactifs d'identification et les principales méthodes de séparation. L'ouvrage se termine par la marche de l'analyse pour les solutions et pour les solides.

Un succès de plus à l'actif du Professeur CHARLOT. On s'étonne que des livres ayant une si grande valeur n'aient pas encore été traduits en anglais et en allemand.

D. MONNIER (Genève)

Gmelins Handbuch der anorganischen Chemie 8. Auflage 1957. Verlag Chemie, GMBH, Weinheim.
Systemnummer 28: Calcium, Teil A, Lieferung 2, 420 Seiten, Kart. DM 232.—.
Systemnummer 68: Platin, Teil D, Gesamtlieferung, 638 Seiten, Kart. DM 370.—.

Wohl jedermann der zum ersten male einen Band *Gmelins Handbuch der anorg. Chemie* in die Hände bekommt, ist überrascht durch die Fülle von Wissen das in diesen Büchern zusammengetragen ist. Man bekommt bei ihrer Lekture das bestimmte Gefühl, es handle sich hier nun tatsächlich um eine lückenlose Dokumentation und Beschreibung des behandelten Gebietes.

In ganz demselben Rahmen halten sich auch die beiden Bände der Neuauflage, die in der Folge kurz beschrieben werden sollen.

Calcium: Vorkommen, Das Element, Die Legierungen

Das Buch beginnt mit einer umfassenden Aufzählung der bekannten Vorkommen des Elementes im Kosmos. Man findet z.B. die Resultate über Häufigkeitsmessungen auf der Erde, den Planeten, der Sonne und in den Sternspektren.

Im folgenden Abschnitt ,,Geochemie", sind die Erscheinungsformen der Calciummineralien und ihre Häufigkeit in der Erdrinde, Lithosphäre, Hydrosphäre, Atmosphäre und Biosphäre behandelt.

Daran schliesst eine Aufzählung der Lagerstätten der Calciummineralien auf der ganzen Welt. Man findet besondere Kapitel für die technisch wichtigen Lagerstätten von Flusspat, Gips, Islandspat und Calciumphosphat. Jedes Kapitel ist für sich nach den verschiedenen Erdteilen und den einzelnen Ländern geordnet. Man erhält dadurch sehr leicht einen umfassenden Überblick über die verschiedenen Vorkommen.

In einem kleinen Kapitel wird man über Vorkommen, die Entstehung, den chemischen und physikalischen Eigenschaften der übrigen Calciummineralien orientiert.

Das Metall Calcium nimmt infolge seinem etwas geringen Interesse einen relativ kleinen Raum des Buches ein (100 Seiten). Das Kapitel behandelt zuerst die Gewinnung des Metalles. Besonders wertvoll dürften die Angaben in Bezug der seltenen Isotopen des Ca sein. Dann sind der Reihe nach die physikalischen, die elektrochemischen und chemischen Eigenschaften behandelt. Ein besonders interessanter kleiner Abschnitt befasst sich mit der physiologischen Wirkung des Ca und seiner Verbindungen.

Platin: Komplexverbindungen mit neutralen Liganden

Das Buch erläutert einleitend die Klassifikation, Nomenklatur und Schreibweise der Formelen des beachtlichen Stoffgebietes das in dem vorliegenden Bande behandelt ist.

Die Tatsache, dass in dem Hauptteile des Buches gegen 3000 Verbindungen knapp und doch ausführlich behandelt sind, machen ein ganzes System, zum Teil neuartiger Schreibweisen, Abkürzungen und Konfigurationen darstellende Zeichen (auch im Raum) notwendig. Die Erläuterung hierzu findet sich in der Einleitung des Buches, deren eingehende Lekture deshalb einfach unerlässlich ist. Dabei wird einem mehr und mehr klar, dass sich unter dem Titel „Einleitung" ein wahres Kleinod von allgemeinem Interesse verbirgt. Die Natur der koordinativen Bindung, die Eigenschaften der Liganden und ihre Wirkungen auf ein molekulares System werden behandelt. Dabei wurde dem *trans*-Effekt besonders Rechnung getragen, was für das Verhalten vieler Verbindungen neue Gesichtspunkte und besseres Verständnis der Aktion der verschiedenen Liganden gibt. Die eingehende Behandlung der Fachliteratur bis 1953, mit zahlreichen Hinweisen auf die, der westlichen Welt weniger bekannte Soviet Literatur, macht das Buch noch wertvoller.

Der Hauptteil des Buches ist der Beschreibung (Konstitution, Darstellung, Eigenschaften) der einzelnen Verbindungen gewidmet. Das Material ist übersichtlich nach dem Wert des Zentralatoms und den einzelnen Typen geordnet. Diese Anordnung und das Formelverzeichnis am Schlusse des Buches erleichtern wesentlich das Auffinden jeder beliebigen Verbindung.

H. Keller (Genf)

Die komplexometrische Titration, von Gerold Schwarzenbach, *Die chemische Analyse*, Bd. 45, zweite umgearbeitete und erweiterte Auflage, Verlag Enke, Stuttgart, 1956, 119 Seiten.

Die von G. Schwarzenbach entwickelte Komplexometrie hat sich wegen ihrer vielseitigen Anwendbarkeit in den analytischen Laboratorien schnell eingebürgert. Laufend werden neue Arbeitsweisen entdeckt. So nennt die jetzt vorliegende, zweite Auflage neben den in der ersten Auflage erfaßten 181 Literaturzitaten 133 neue Abhandlungen aus den Jahren 1954 — 1956. Bei dieser Verbreitung der komplexometrischen Methode erscheint es überflüssig, hier auf ihre Grundlagen einzugehen. Selbstverständlich ist auch, daß der Autor, dem man diese Entwicklung verdankt, den Stoff klar und überzeugend darlegt.

Setzt man die Kenntnis der ersten Auflage voraus, so ist von der neuen Auflage folgendes zu sagen: Sie behält die zweckmäßige Gliederung des Stoffes in theoretische Kapitel (51 Seiten) und Arbeitsvorschriften (42 Seiten) bei. Zahlreiche neue Literaturstellen wurden eingearbeitet und führten zu kleineren Ergänzungen. Neue Abschnitte findet man bei den Metallindikatoren (Eriochromazurol S, Eriochromcyanin R, PAN, Zinkon, Dithizon). Eine wichtige Bereicherung der Arbeitsvorschriften stellt ferner die Aluminiumbestimmung dar, die die Rücktitration des Komplexonüberschusses mit Zinksulfat gegen Dithizon verwendet.

Die vorliegende Monographie wird die Verbreitung der komplexometrischen Methoden weiter fördern. Sie kann nur bestens empfohlen werden. Druck und Ausstattung sind gut.

H. Schäfer (Münster)

Mises au point de chimie analytique pure et appliquée et d'analyse bromatologique, publ. sous la direction de J. A. Gautier, 4ème Série., Masson et Cie., Paris, 1956, 212 p., 21 fig. et tabl., Frs. fr. 2400.

Nous avons déjà rendu compte dans cette revue (*Anal. Chim. Acta*, 12 (1955) 499 et 14 (1956) 591) des trois premiers volumes de cette collection; on nous annonce que le cinquième et le sixième se trouvent sous presse. Voici donc un bon départ et une formule heureuse qui maintient sa tradition.

L'article théorique est cette fois donné par Souchay sur la polarographie; il consiste en une bonne mise au point pour débutants dans ce comaine et sans développement mathématique; les exemples choisis pour les dosages concernent des médicaments ou des corps biologiques intéressants; les références citées sont au nombre de 68.

Les conférences spéciales sur des groupes de corps pharmaceutiques ou alimentaires ont été faites cette année par Courtois sur quelques acquisitions récentes dans le domaine de l'analyse des glucides en insistant surtout sur la chromatographie sur colonne et sur papier (72 références). Ensuite Jaulmes et Mlle Hamelle ont parlé de la détermination de l'extrait sec des vins avec reproduction du graphique de Janssens pour la classification de tous les vins spéciaux du monde entier. L'acétylation de la fonction hydroxyle a été développée par Mesnard qui parle des agents acétylants et des techniques (68 références), puis Navellier développe dans le cas du lait, la conservation et l'analyse des échantillons qui est un problème difficile. Enfin, Truhaut étudie très largement le rôle des substances étrangères dans les aliments (avec 265 références) en insistant sur les matières colorantes.

Cette brochure particulièrement intéressante dans la variété et le niveau des sujets traités se fait remarquer aussi par une excellente présentation de la Maison Masson et Cie.

C. Duval (Paris)

OBSERVATIONS ON THE PERMANGANATE-ARSENIOUS OXIDE TITRATION*

by

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It is well known that the direct titration of arsenious oxide with potassium permanganate in dilute acid solution is unsatisfactory because of the slowness of the reaction. LANG[1] found that the titration proceeds rapidly and stoichiometrically with the addition of potassium iodide or potassium iodate catalyst. KOLTHOFF AND SANDELL[2] state that "the titration of arsenious oxide with permanganate in sulfuric acid medium proceeds smoothly at the beginning, but a yellow-green or brown coloration soon appears (complex manganic arsenates) and disappears only slowly, even at high temperatures." The titration may, however, be carried out smoothly in hot hydrochloric acid or better with a catalyst in cold hydrochloric acid.

Many of the reactions of permanganate are characterized by an induction effect. One explanation for this effect is that the reduced form of the oxidant acts as a catalyst for the oxidation. This induction effect is then due to the finite time needed for the first production of manganous ion. Once manganous ion is formed, it reacts with permanganate to form manganic ion, which state appears to be responsible for the oxidation. The reaction between manganous ion and permanganate to form trivalent manganese in acid solution is the basis of a potentiometric titration[3,4].

BELCHER AND WEST[5] have measured the formal potential of the manganous-manganic couple in sulfuric acid medium and report it to be within 30 mV of the standard potential of the manganous-permanganate couple as reported by LATIMER[6]. These potentials suggest that the manganic ion is responsible for the oxidation in permanganate reactions. Weight is lent to this suggestion by the existence of the induction effect in permanganate reactions. Oxidation by permanganate, which exhibits an initial slow reaction, requires the complete destruction of the radical while oxidation by manganic ion, which involves transfer of electrons only, has been shown to be rapid[5]. If the manganic ion is actually responsible for the oxidation in permanganate reactions in acid solution, this would explain the induction effect. Potentiometric studies, however, are precluded by the closeness of the potentials involved.

The present investigation was undertaken to study the nature of the trivalent manganese complex formed during the permanganate–arsenious oxide reaction.

Reagents and apparatus

The reagents used were all of "analytical grade". The approximately decinormal potassium permanganate solutions were standardized against arsenious oxide using potassium iodate as catalyst. The solutions were stored in the dark and the titre was checked twice weekly.

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* Taken in part from the master's dissertation by ANTHONY V. DeTHOMAS, University of Connecticut, Storrs, Conn., June 1957.

Optical measurements were made in the Beckman Model B spectrophotometer using 1 cm Corex cells and polarographic studies were carried out on the Leeds and Northrup Electrochemograph, Type E.

Experimental procedures

Two general experimental procedures were adopted involving the formation of manganic ion by (a) the reduction of permanganate and (b) the oxidation of manganous ion, respectively.

(a) To a 50 ml aliquot portion of an arsenious oxide solution, containing about 0.25 g of the oxide, was added an amount of concentrated acid calculated to make the solution of the desired acidity after the addition of 25 ml of approximately decinormal potassium permanganate. The solution was then transferred to a 200 ml volumetric flask and diluted to the mark with acid of the same concentration as that chosen.

(b) To approximately 0.30 g of a manganous salt was added an amount of solid lead dioxide in excess of the theoretical amount needed to oxidize the manganese to the trivalent state. The mixture was then transferred to a 50 ml volumetric flask and diluted to the mark with acid of the desired concentration.

The solutions were thoroughly mixed and due to the transient nature of the colors, were examined immediately in the spectrophotometer. In those cases where the solution contained suspended material, a rapid filtration through a sintered-glass funnel was performed prior to absorption measurements.

RESULTS

Sulfuric acid medium

The reduction of permanganate with arsenious oxide was carried out in solutions of sulfuric acid ranging in final concentration from 0.01 to 10*M*. The solution 0.01*M* in sulfuric acid developed the brown turbidity of manganese dioxide upon the addition of the potassium permanganate solution. The 0.1*M* solution produced a bright green color which faded to colorless in about six minutes. The absorption spectrum of this solution, having a maximum at 600 mμ is shown in Fig. 1.

All other solutions developed a pink color which rapidly faded to colorless (four to five minutes). The solutions 5 to 9*M* in sulfuric acid, however, were somewhat more stable and a typical spectrum in this range is shown in Fig. 2. This spectrum exhibits a maximum in the vicinity of 500 mμ and compares favorably with the spectrum of the manganic sulfate complex obtained by PURDY AND HUME[7].

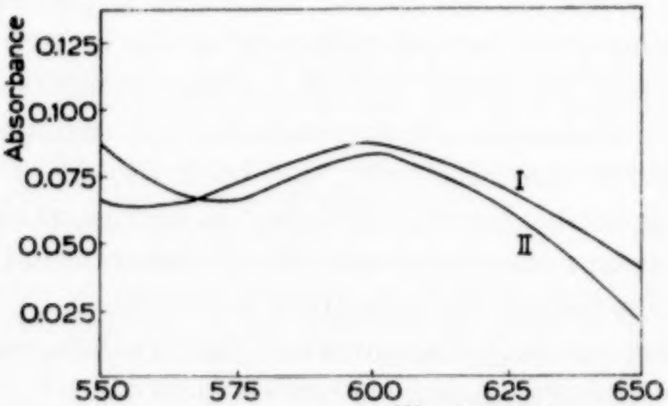


Fig. 1. Absorption spectra of the manganic arsenate complex.
Curve I – in 2*M* perchloric acid.
Curve II – in 0.1*M* sulfuric acid.

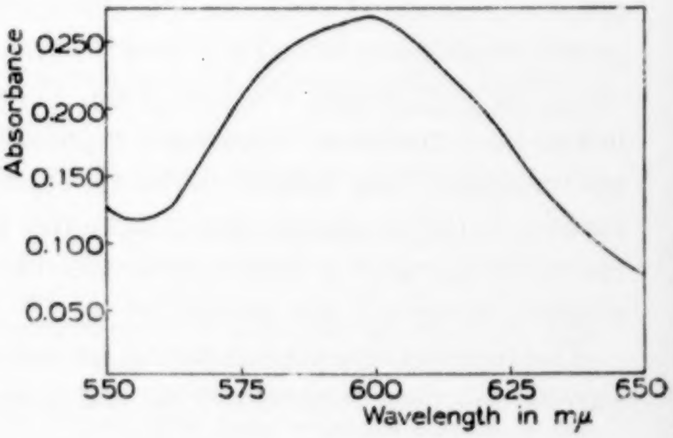
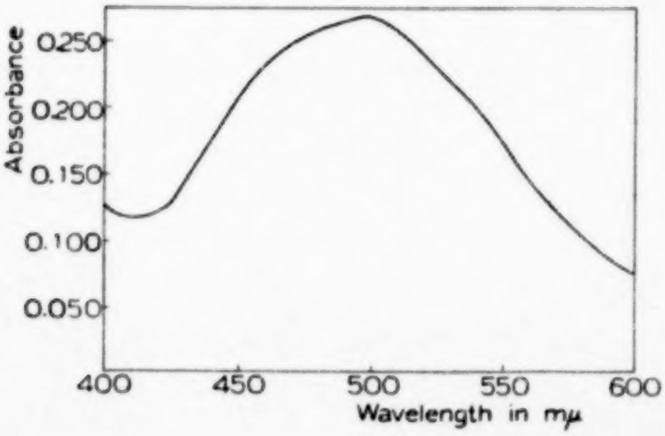


Fig. 2. Absorption spectrum of the manganic sulfate complex in 6*M* sulfuric acid.

ERRATUM

Anal. Chim. Acta, Vol. 18 (1958), page 186, Fig. 2.
In the original Fig. 2 the horizontal scale was incorrectly given. The new figure printed below gives the correct scale.



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Next manganous sulfate was oxidized by lead dioxide in solutions of sulfuric acid at various concentrations. No color developed in the solutions 0.01 to 0.1*M* in acid. A pink color was obtained in the solutions 1 to 9*M* in acid and the spectra of these solutions were the same as the spectra obtained for the permanganate reduction with arsenious oxide. Since this pink color is formed in a solution containing only sulfate anions, the color must be due to the manganic sulfate complex. A solution of permanganate in 6*M* sulfuric acid exhibits no absorbance peaks between 500 and 600 mμ.

The average loss of absorbance for solutions of the manganic sulfate complex was found to be 0.13 and 0.24 absorbance units after 1 and 2 days respectively.

The green color obtained by reducing permanganate with arsenious oxide in 0.1*M* sulfuric acid could be due either to a hydrated sulfate complex or an arsenite or arsenate complex of trivalent manganese. The first possibility, *i.e.* the hydrated sulfate complex, was ruled out since the green color never formed unless arsenate ion was present in the solution. Manganous sulfate was oxidized with lead dioxide in perchloric acid medium and the solutions were made up to contain equimolar amounts of sulfate and arsenate ion. A green color was obtained in all the solutions 1 to 8*M* in acid and the spectra of these solutions were the same as the spectrum of the green solution above. Since there was no arsenite present in the solution, the green color must be a manganic arsenate complex.

Both procedures, *i.e.* the reduction of permanganate and the oxidation of manganous ion, were then carried out in solutions of sulfuric acid containing equimolar amounts of sulfate and arsenate ion. In the former procedure, the manganic sulfate complex was formed in all solutions. In the latter procedure, however, the 0.01*M* acid solution was colorless and the 0.1 and 1.0*M* acid solutions were pink. This pink coloration was identified as the manganic sulfate complex and was found to lose about 0.01 absorbance units in 30 minutes. The solutions 2 to 4*M* in acid developed the green color of the manganic arsenate complex.

Perchloric acid medium

The above experiments were repeated in perchloric acid medium since perchlorate ion shows little or no tendency to form complexes[8]. The brown turbidity of manganese dioxide developed when permanganate was reduced with arsenious oxide in 0.05*M* perchloric acid. The manganic arsenate complex was obtained in solutions 1 to 7*M* in acid. Since the absorbance of these solutions was very low, a more concentrated solution of this complex was prepared and its spectrum is shown in Fig. 1.

Manganous sulfate oxidized with lead dioxide in perchloric acid of various concentrations develops the manganic sulfate complex. However, when sufficient solid sodium arsenate is added to the solution to make equimolar the concentration of sulfate and arsenate ions, the manganic arsenate complex is formed. It therefore appears that when sulfate and arsenate have an equal opportunity to compete for the trivalent manganese, it is the arsenate complex formation which predominates.

Substitution of manganous chloride for manganous sulfate and addition of excess arsenate ion results in the production of a pale yellow color in solutions 0.05 to 0.1*M* in perchloric acid. The manganic arsenate complex was obtained in solutions 1 to 4*M* in acid and an amber color was formed in solutions 5 to 8*M* in acid. This amber color faded rapidly to yellow. The amber color is believed to be a transient chloro-complex of trivalent manganese. The pale yellow color was identified as dissolved chlorine.

Other studies

The reduction of permanganate with arsenious oxide in hydrochloric acid medium results either in the formation of manganese dioxide or of the manganic chloride complex. With acidities less than 0.1M, manganese dioxide was formed and in solutions 1 to 7M in acid, the chloro-complex was formed.

Polarograms were run on solutions containing the manganic sulfate complex. These solutions were prepared both by the oxidation of manganous ion with lead dioxide and by the reduction of permanganate with arsenious oxide. The acid medium in each case was 2M perchloric acid. Two small waves were obtained having half-wave potentials of —0.43 and —0.87 V *vs.* S.C.E. Polarograms run on the manganic arsenate complex also displayed two waves, —0.35 and —0.83 V respectively. In both cases, the height of the second wave was about double the height of the first wave.

Undue emphasis cannot be placed on these polarograms since (1) the complexes are markedly unstable, (2) the supporting electrolytes were necessarily different, and (3) interferences from catalytic hydrogen could not be eliminated without destroying the complexes. The studies do show, however, that there are two different complexes which can exist with only minor changes to the system under study.

Attempts at extracting the complexes into a wide variety of organic solvents proved fruitless and the absorption spectrum of the solvent remained the same before and after the extraction procedure.

Because of their marked instability, the determination of the formulae of the complexes by the method of continuous variations[9] or molar ratios[10] was abandoned.

The results of this work indicate that the most stable intermediate formed during the permanganate–arsenious oxide reaction is a complex of trivalent manganese. The nature of this complex depends upon the composition of the reaction solution.

ACKNOWLEDGEMENT

The authors are indebted to the U.S. Atomic Energy Commission for partial support of this work.

SUMMARY

The reduction of permanganate and the oxidation of manganous ion have been studied in a variety of acid solutions. The product appears to be an unstable complex of trivalent manganese. The manganic sulfate complex is pink in solution and the manganic arsenate complex is green. Complexes prepared in hydrochloric acid were found to be highly unstable and decomposed rapidly with the formation of free chlorine. The results of this work shed some light on the mechanism of the permanganate–arsenious oxide titration.

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THE DETERMINATION OF THE GAMMA ISOMER CONTENT OF HEXACHLORCYCLOHEXANE DIPWASHES

by

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INTRODUCTION

It is well known that the biological efficiency of hexachlorcyclohexane (BHC) dipwashes depends mainly upon the gamma isomer content. Normally a total BHC analysis, which has the advantage of being rapid and simple, is employed to measure the efficiency of a used dipwash. This presupposes that the ratio of gamma isomer to total BHC remains constant, an assumption which is open to doubt[1,2].

In order to obtain a more reliable measure of the biological efficiency, a method for determining the gamma isomer content was required. Chromatographic and polarographic procedures were tried; the former was too laborious for routine work and the latter failed to give satisfactory results. Consequently attention was turned to the cryoscopic method of BOWEN AND POGORELSKIN[3]. The method involves dissolving a known weight of the sample in a twenty-fold excess of pure gamma BHC and measuring the depression of freezing point of the solvent. The isomers other than gamma in the sample, all having the same molecular weight, cause similar depressions of the freezing point, according to the usual equation.

$$T = \frac{1000KW_2}{M_2W_1} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

The gamma isomer in the sample has no effect on the freezing point of the solvent, consequently the amount present can be calculated from the depression of freezing point caused by the sample.

If the sample is impure, as in the case of dipwash extracts, the above method cannot be applied as the effective molecular weight of the sample is unknown. This difficulty was overcome by obtaining a figure for the effective molecular weight from the depression of the freezing point using benzene as solvent. From this and the freezing point depression in gamma BHC solvent the gamma isomer content of the sample can be calculated.

Although this method has only been applied to the determination of the gamma isomer in impure BHC the principle of the method should be applicable in many cases where the determination of one component in a multi-component mixture is required.

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THEORETICAL

The basis for the calculation is as follows:

If M = effective molecular weight of sample,
W_2 = weight of sample,
W_{gamma} = weight of gamma isomer in sample,
W_{BHC} = weight of BHC other than gamma in sample,
W_{imp} = weight of impurities,
M_{imp} = effective molecular weight of impurities,
and M_{BHC} = molecular weight of BHC,

then

$$\frac{W_2}{M} = \frac{W_{\mathrm{gamma}}}{M_{\mathrm{BHC}}} + \frac{W_{\mathrm{BHC}}}{M_{\mathrm{BHC}}} + \frac{W_{\mathrm{imp}}}{M_{\mathrm{imp}}} \tag{2}$$

M is given by

$$M = \frac{1000KW_2}{TW_1} \tag{3}$$

where K = cryoscopic constant of benzene,
W_1 = weight of benzene,
T = depression of the freezing point of benzene.

If W_2 g of sample is dissolved in W_1 g of pure gamma BHC and the depression of freezing point T^1 measured, then

$$M^1 = \frac{1000K^1(W_2 - W_{\mathrm{gamma}})}{T^1\,(W_1 + W_{\mathrm{gamma}})} \tag{4}$$

where K^1 = cryoscopic constant of gamma BHC,
and M^1 = effective molecular weight of the substances other than gamma BHC of the sample.

Now,

$$\frac{W_2 - W_{\mathrm{gamma}}}{M^1} = \frac{W_{\mathrm{BHC}}}{M_{\mathrm{BHC}}} + \frac{W_{\mathrm{imp}}}{M_{\mathrm{imp}}} \tag{5}$$

(similar to (2) above).

From (4)

$$\frac{W_2 - W_{\mathrm{gamma}}}{M^1} = \frac{T^1\,(W_1 + W_{\mathrm{gamma}})}{1000K^1} \tag{6}$$

From (2) and (5)

$$\frac{W_2 - W_{\mathrm{gamma}}}{M^1} = \frac{W_2}{M} - \frac{W_{\mathrm{gamma}}}{M_{\mathrm{BHC}}} \tag{7}$$

Solving (6) and (7)

$$W_{\mathrm{gamma}} = \frac{M_{\mathrm{BHC}}(1000K^1W_2 - MT^1W_1)}{M(1000K^1 + M_{\mathrm{BHC}}T^1)} \tag{8}$$

Finally, from (3) and (8),

$$W_{\mathrm{gamma}} = \frac{290.8W_1(K^1T - KT^1)}{K(1000K^1 + 290.8T^1)} \tag{9}$$

Thus the weight of gamma isomer in the sample, W_{gamma}, can be calculated from a knowledge of the cryoscopic constants of the solvents and from determinations of the depression of the freezing points. Equation (9) is valid only if the same or nearly the same weight, W_2 g, of sample is dissolved in the same or nearly the same weight, W_1 g, of solvent.

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EXPERIMENTAL

Reagents

(a) Benzene: Analytical Reagent grade, containing sodium wire.
(b) Pure gamma BHC: 200 g lindane is recrystallised from acetone (1 ml/g), filtered and dried between filter paper. The product is recrystallised from *n*-hexane (5 ml/g), filtered and dried at about 100°C for several hours.
(c) Pure alpha BHC: 50 g technical BHC (about 70% alpha) is shaken with 150 ml methanol for thirty minutes and filtered with suction. The residue (alpha and a little beta) is recrystallised from toluene (2 ml/g) until a melting point of 157-158°C is attained.
(d) Chromic acid: prepared by addition of 98% sulphuric acid to saturated sodium chromate until the precipitate formed dissolves and remains in solution on cooling.
(e) Ether: technical grade redistilled.

*Freezing point measurements**

(a) *Determination of cryoscopic constant of benzene.* 3 ml (about 2.6 g) of benzene was added to a freezing point tube (120 × 16 mm test tube) fitted with a thermometer and motor-driven loop stirrer. The tube was placed in an air jacket surrounded by an ice-bath. The stirrer was driven at about 100 strokes per minute and the highest temperature reached after supercooling was noted. The determination was repeated until two readings differing by not more than 0.01°C were obtained.

A 0.13 g sample of alpha BHC was weighed accurately into a freezing point tube, 3 ml of benzene introduced and the tube reweighed. The mixture was cooled to about 10°C, to minimise evaporation of benzene, stirred until the BHC dissolved and the freezing point determined as above. The cryoscopic constant was calculated from equation (1).

(b) *Determination of cryoscopic constant of gamma BHC.* 2.6 g pure gamma BHC was weighed into a freezing point tube, fitted with a thermometer and motor-driven loop stirrer. The sample was heated to about 125°C over a low flame, the tube was quickly placed in an air jacket surrounded by boiling toluene and allowed to cool with mechanical stirring. At the expected freezing point (112.4°C) the sample was seeded with a small crystal of gamma BHC to prevent severe supercooling. The freezing point of a mixture of 0.13 g alpha BHC and 2.6 g BHC was similarly determined and the cryoscopic constant calculated. Typical results are shown in Table I.

TABLE I

CRYOSCOPIC CONSTANTS OF BENZENE AND GAMMA BHC

Freezing point of benzene (°C)	4.95, 4.95, 4.95
Weight of alpha BHC (g)	0.130
Weight of benzene (g)	2.629
Freezing point of solution (°C)	4.08, 4.08, 4.05, 4.08
K	5.10
Freezing point of pure gamma BHC (°C)	112.42, 112.48, 112.47, 112.48
Weight of alpha BHC (g)	0.131
Weight of gamma BHC (g)	2.601
Freezing point of solution (°C)	109.54, 109.58, 109.57, 109.58
K	16.8

Determination of gamma BHC content of synthesised samples

Impurities similar to those in BHC dipwashes were obtained by extraction of used DDT miscible oil dipwashes with benzene and evaporation of the solvent. The weighed residue was dissolved in ether and made up to 50 ml. Aliquots of this solution were added to freezing point tubes containing known amounts of alpha and gamma BHC and the ether evaporated by partial immersion of the tube in the refluxing toluene bath. The freezing point depressions when identical samples were dissolved in benzene and in gamma BHC were determined as previously described, and the gamma BHC contents calculated from equation (9).

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* The determinations were carried out with due regard to the usual precautions[4]. The thermometers used were capable of being read to 0.01°C.

TABLE II

GAMMA BHC CONTENT OBTAINED FOR KNOWN SAMPLES

W_{gamma} present (g)	0.027	0.026	0.020	0.000
W_{alpha} present (g)	0.082	0.081	0.088	0.099
W_{impurity} present (g)	0.017	0.025	0.025	0.023
W_2 (= $W_{\text{gamma}} + W_{\text{alpha}} + W_{\text{impurity}}$)	0.126	0.132	0.133	0.122
W_1 (= wt. of benzene, g)	2.640	2.743	2.645	2.630
W_1 (= wt. of gamma BHC, g)	2.640	2.745	2.626	2.628
T (°C)	0.78	0.80	0.85	0.80
M = (effective mol. wt. of sample)	342	307	302	296
T^1 (°C)	1.90	2.05	2.33	2.53
W_{gamma} found (g)	0.030	0.027	0.021	0.005

The agreement between the gamma BHC content found and that present was satisfactory, and the method was finally applied to dipwashes.

Dipwash analyses

Four used BHC powder dipwashes of known total BHC content were available for analysis; the technique employed was as follows.

Approximately 20 ml chromic acid was added to 400 ml of the dipwash to precipitate the BHC and to destroy as much impurity as possible. The mixture was centrifuged, filtered and the residue extracted with ether. The extract was evaporated to dryness on a steam bath and weighed (W g), redissolved in ether, and the solution made up to 25 ml. Two aliquots, each calculated (from W) to contain 0.130 g impure BHC were evaporated to constant weight, in freezing point tubes partially immersed in boiling toluene, and the gamma BHC content determined as for the synthetic samples. When heating to evaporate ether, care was taken to avoid loss of BHC by sublimation. The results, which agreed well with those obtained by chromatography, are given in Table III.

TABLE III

DIPWASH ANALYSES

Sample	*Gamma BHC contents (% of total BHC)*	
	By cryoscopy	*By chromatography*
A	10	figure not available
B	14	14.8
C	14	13.5
D	14	13.5

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SUMMARY

The gamma BHC content of dipwashes has been determined satisfactorily by a cryoscopic method. The dipwash is treated with chromic acid to precipitate the total BHC and to destroy much of the organic impurity. Portions of the isolated impure BHC are dissolved in both benzene and pure gamma BHC. By measurement of the resultant freezing point depression of the solvents, the proportion of gamma isomer in the original sample can be calculated. The principle of the method should be applicable to other systems where the determination of one component in a multi-component mixture is required.

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CIRCULAR-PAPER CHROMATOGRAPHY IN THE SEPARATION OF IONS

SEPARATION OF PRECIOUS METALS

by

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Circular-paper chromatography, commonly known as Rutter's technique as he was the first to apply it to the separation of inorganic ions, was introduced in 1939 by BROWN[1] and it was found to be a very convenient analytical tool for the detection and separation of both organic and inorganic ions[2]. In spite of its sensitivity, resolving power and reproducibility, no attempt had yet been made to utilise it for the separation of the precious metals, Pd, Pt, Ir, Rh, Ru, Os and Au. MAJUMDAR AND CHAKRABARTTY[3], with electro-chromatography as their tool, succeeded in separating several ternary and quaternary mixtures of precious metals, even when microgram quantities (15-20 μg) of each ion were present in the mixture.

As a simple and more rapid procedure for the separation and identification of the said metals when present in traces, the technique of circular paper chromatography has been found to be highly effective for separating three or four such ions from a mixture into distinct circular zones. This paper presents the results of a systematic study of their separation with several mixtures of solvents.

EXPERIMENTAL

Preparation of solvents

The solvents (A to P) were prepared by mixing different ingredients in the proportions given below.

A. *tert.*-Butyl alcohol (70 ml), hydrochloric acid (10 ml, sp.gr. 1.19) and water (20 ml).
B. Acetone (70 ml), hydrochloric acid (10 ml, sp.gr. 1.19) and water (20 ml).
C. *tert.*-Butyl alcohol (70 ml), acetic acid (10 ml, sp.gr. 1.055) and water (20 ml).
D. Acetone (70 ml), acetic acid (10 ml, sp.gr. 1.055) and water (20 ml).
E. *tert.*-Butyl alcohol (70 ml), acetic acid (10 ml, sp.gr. 1.055), ammonium iodide (2 g) and water (20 ml).
F. Acetone (70 ml), acetic acid (10 ml, sp.gr. 1.055), ammonium iodide (2 g) and water (20 ml).
G. *tert.*-Butyl alcohol (50 ml), acetone (20 ml), hydrochloric acid (10 ml, sp.gr. 1.19) and water (20 ml).
H. *tert.*-Butyl alcohol (50 ml), acetone (20 ml), acetic acid (10 ml, sp.gr. 1.055) and water (20 ml).
I. Acetone (50 ml), *tert.* – butyl alcohol (20 ml), hydrochloric acid (10 ml, sp.gr. 1.19) and water (20 ml).
J. Acetone (50 ml), *tert.* – butyl alcohol (20 ml), acetic acid (10 ml, sp.gr. 1.055), ammonium iodide (2 g) and water (20 ml).
K. *tert.*-Butyl alcohol (35 ml), acetone (35 ml), hydrochloric acid (10 ml, sp.gr. 1.19) and water (20 ml).
L. *tert.*-Butyl alcohol (35 ml), acetone (35 ml), acetic acid (10 ml, sp.gr. 1.055), ammonium iodide (2 g) and water (20 ml).

TABLE I

R_{max} AND R_{min} VALUES OF THE PRECIOUS METALS AT 20-25°C

Solvent	Time in hours	Pd		Pt		Ir		Rh		Ru		Os		Au	
		R_{max}	R_{min}	R_{max}	R_{min}	R_{max}	R_{min}	R_{max}	R_{min}	R_{max}	R_{min}	R_{max}	R_{min}	R_{max}	R_{min}
A	2	0.90	0.81	0.96	0.87	0.50	0.30	0.48	0.32	0.25	0.13	1.00	0.84	1.00	0.96
B	1	1.00	0.98	1.00	0.97	0.50	0.41	0.65	0.56	0.40	0.32	1.00	0.96	1.00	0.98
C	2	0.42	0.25	0.24^{d}	0.14^{d}	0.40	0.27^{d}	0.28	0.00	0.19	0.08	0.21	0.00	0.92	0.78
D	1	0.90	0.86	0.81	0.76	0.46	0.27	0.41	0.14	0.31	0.23	0.86	0.84	0.98	0.96
E	2	0.61	0.58	0.82	0.79	0.51	0.40	0.32^{d}	0.00	0.22	0.09	0.33	0.26	0.78	0.68
				0.64^{d}	0.48^{d}										
F	1	1.00	0.90	0.70	0.65	0.58	0.40	0.28	0.22	0.25	0.19	0.84	0.80	1.00	0.87
								0.14	0.09						
G	2	1.00	0.94	1.00	0.94	0.59	0.40	0.54	0.39	0.35	0.20	1.00	0.93	1.00	0.93
H	2	0.80	0.75^{d}	0.76	0.71^{d}	0.46	0.33^{d}	0.32^{d}	0.00	—	—	1.00	0.94	0.90	0.76^{d}
		0.40	0.35	0.24	0.17	0.16	0.11								
I	1	1.00	0.94	1.00	0.94	0.58	0.48	0.73	0.50	—	—	1.00	0.94	1.00	0.92
J	1	1.00	0.85	0.83	0.74	0.70	0.64	0.46	0.37	—	—	0.85	0.81	1.00	0.84
						0.61	0.49	0.30	0.12						
K	2	1.00	0.97	1.00	0.97	0.53	0.35	0.53	0.40	0.36	0.28	1.00	0.97	1.00	0.98
L	2	1.00	0.75	0.80^{d}	0.70^{d}	0.67	0.63	0.39	0.33	—	—	0.85	0.80^{d}	0.72	0.60
						0.53	0.49	0.24	0.10						
M	1	0.33	0.14	0.25^{d}	0.10	0.77	0.71	0.51	0.46	0.38	0.34	1.00	0.90	0.08	0.00
						0.13	0.08	0.33	0.31			0.20	0.00		
								0.15	0.10^{d}						
N	1	0.70	0.61	0.12	0.00	0.92	0.82	0.38	0.32	0.11	0.00	0.35	0.00	1.00	0.87
								0.16	0.11						
O	2	0.54	0.46	0.17^{d}	0.11	0.73	0.60	0.35	0.30	0.28	0.17	0.23	0.00	0.92	0.80
								0.20	0.00						
P	2	0.40	0.13	0.21	0.10^{d}	0.90^{d}	0.00	0.40	0.37	0.32	0.30	0.29	0.22	0.16	0.00
								0.18	0.00						

M. Acetone (70 ml), ammonia (10 ml, sp.gr. 0.888) and water (20 ml).
N. Acetone (70 ml), ammonia (10 ml, sp.gr. 0.888), ammonium iodide (2 g) and water (20 ml).
O. *tert.*-Butyl alcohol (70 ml), ammonia (10 ml, sp.gr. 0.888), ammonium iodide (2 g) and water (20 ml).
P. *tert.*-Butyl alcohol (70 ml), ammonia (10 ml, sp.gr. 0.888) and water (20 ml).

Procedure

Two parallel cuts, about 0.3 cm apart, were made from the same edge up to the centre of a Whatman No. 1 circular filter paper of 12.5 cm in diameter and the tail so formed was bent at the joint perpendicular to the plane of the paper and cut down to about 1.5 cm in length. Solutions of the chlorides of Pd^{+2}, Pt^{+4}, Ir^{+4}, Rh^{+3}, Ru^{+3}, Os^{+4} and Au^{+3} of approximately the same strength were used and about 0.01 ml of a ternary or a quaternary mixture containing 15-20 μg of each ion was spotted on the centre of the paper. The spot was dried in air for 15 minutes and the paper was placed over a Petri dish containing 10 ml of the developing solvent in such a way that the tail of the wick just dipped into the solvent. The paper was then covered with another Petri dish of the same diameter and placed inside a bell jar. After the development, the paper was dried and the zones were located by spraying with suitable chromogenic reagents.

To judge the possibility of separations, the circular R_{max} and R_{min} values, calculated from the following relations are recorded in Table I. The ions that could not be detected are shown by dashes and the symbol 'd' represents diffuse bands.

$$R_{\text{max}} = \frac{\text{distance from the initial spot to the leading edge}}{\text{distance from the initial spot to the solvent front}},$$

$$R_{\text{min}} = \frac{\text{distance from the initial spot to the trailing edge}}{\text{distance from the initial spot to the solvent front}}.$$

The results of Table I were checked by repetition and found to be reproducible. On the basis of these results, separations of three-, four- and five-component mixtures of the precious metals that appeared to be possible were tried. The sequences of separation obtained thereby are recorded in Table II. The square brackets indicate that the enclosed ions have a portion of their migration zone in common.

TABLE II

Solvent	*Sequence of separation*
A	Au–Pd–Rh–Ru, Au–Pd–Ir–Ru, Os–Rh–Ru, Os–Ir–Ru, Pt–Rh–Ru, Pt–Ir–Ru
B	Os–Rh–[Ir–Ru], Pt–Rh–[Ir–Ru], Pd–Rh–[Ir–Ru], Au–Rh–[Ir–Ru]
D	Au–Os–Ir, Au–Os–Rh, Au–Pd–Ir, Au–Pd–Rh, Au–Pt–Ir, Au–Pt–Rh
E	Au–Pd–Ir–Ru, Au–Pd–Ir–Os, Au–Pd–Ir–Rh
F	Pd–Os–Ir–Rh, Pd–Os–Ir–Ru, Pd–Pt–Ir–Rh, Pd–Pt–Ir–Ru, Au–Pt–Ir–Rh, Au–Pt–Ir–Ru
L	Pd–Ir–Rh, Os–Ir–Rh
N	Au–Pd–Pt, Au–Pd–Rh, Ir–Pd–Pt, Ir–Pd–Rh
O	Au–[Ir–Pd]–Os, Au–[Ir–Pd]–Pt, Au–[Ir–Pd]–Rh

In spite of our repeated attempts, the separations of Au - Pd - Ru developed with the solvent C, of Au - Pd - Ru, Au - Os - Ru and Au - Pt - Ru with solvent D and of Au-Pd - Ru, Ir - Pd - Ru, Au - Pd - Os, Ir - Pd - Os with solvent N could not be achieved since Ru in the cases of C, D and N and both Ru and Os in the case of N did not give distinct colour reactions with any of the spot testing reagents. Separations of Au - Pd - Pt - Ir, Au - Pd - Pt - Rh and Au - Pd - Pt - Ru with the solvent D and of Pd - Os - Pt - Ir - Rh and Pd - Os - Pt - Ir - Ru with the solvent F also failed owing to complete overlapping of Pd and Pt in the case of D and Os and Pt in the case of F.

DISCUSSION

For a systematic study of the separation of the precious metals, mixtures of solvents are prepared containing a mineral acid, an organic acid, a volatile solvent and a less volatile solvent, *e.g.* a mixture of hydrochloric acid, acetic acid, acetone and *tert.*-butyl alcohol. When acetone is the major component of a mixture, it is found that, owing to its volatility, a development period of one hour is sufficient for effective separation. When *tert.*-butyl alcohol is present in the solvent mixture, however, two hours are required for development. A mixture of *tert.*-butyl alcohol and acetone, in various proportions, does not give effective results. In several mixtures, ammonium hydroxide and/or ammonium iodide is added as complexing agent to study the behaviour of precious metals. Since the chloro- and the iodo-complexes of precious metals are anionic, higher R_F values are noticed and this is specially so in the case of Pd, Pt, Os and Au. The observation of MACNEVIN AND CRUMMETT[4] that the palladium ammine complex is more stable than the iridium ammine complex, if formed at all, is corroborated by our results, though few, which show that the R_F values of Pd are always smaller than those of Ir. Based on the fact that competition takes place between the halide and the ammonia for the precious metals, attempts have been made to separate them by adding both ammonium hydroxide and ammonium iodide. The formation of more than one band, pronounced in the cases of Ir and Rh, may be due to a change in the valency of the metallic ions and/or due to soluble complex and insoluble simple compound formation (*cf.* MAJUMDAR AND CHAKRABARTTY[3]). Failure to detect the presence of Ru and Os in solvents C, D and N is perhaps due to the fact that the products resulting from hydrolysis with acetic acid (without ammonium iodide) or ammonia, are not responsive to spot testing reagents.

SUMMARY

A circular-paper chromatographic method for separating the precious metals Pd^{+2}, Pt^{+4}, Ir^{+4}, Rh^{+3}, Ru^{+3}, Os^{+4} and Au^{+3}, using several solvent mixtures with or without complexing agents, has been studied. Mixtures of microamounts of three or four of these metals can be effectively separated into distinct circular zones within one or two hours.

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SALTING-OUT CHROMATOGRAPHY

III. ALIPHATIC AND POLYGLYCOL ETHERS, CARBOXYLIC ACIDS

by

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The authors have shown that the analysis of complex mixtures of alcohols[1], polyglycols[2], and amines[3] is facilitated by salting-out chromatography, a process whereby water-soluble nonelectrolytes are separated by elution through a column of ion-exchange resin with a concentrated salt solution as eluent. The logarithm of the distribution ratio of the nonelectrolyte was shown[1] to increase linearly with the molarity of salt in the eluent solution, and the slope of the line was found to be identical with the salting-out constant obtained from solubility measurements. In this report, salting-out chromatography is applied to the separation of aliphatic and polyglycol ethers. A brief description of the attempt to utilize this technique for the separation of the aliphatic acids is included.

EXPERIMENTAL

The details for the preparation of columns of the ion-exchange resin and the procedures for the elution are given in ref.[1]. Effluent fractions of 6.0 ml were analyzed by oxidation with dichromate in 50% sulfuric acid with subsequent measurement of the absorbance of Cr(III)[1,4].

Interstitial volumes

The interstitial or void volume V of a column of ion-exchange resin was determined by the procedure which follows[5]. Slurry the hydrogen form of the resin with water and pour into a glass tube[1] whose internal cross-sectional area is known. After 5 minutes, drain off the excess liquid to the top of the bed. After percolation of at least 1 l of 0.100N hydrochloric acid through the resin, again drain to the top of the bed and record the height of the column. Remove the stopcock at the bottom of the column and wash the bottom of the sintered glass disk to remove any hydrochloric acid that is not present in the bed of resin. Wash the acid from the resin bed with a sufficient quantity of water and collect the effluent in a suitable volumetric flask. The milliequivalents of acid in the effluent, found by titration with sodium hydroxide, is then divided by the normality of the acid to find the interstitial volume.

Ethers

The ethers used in this investigation are listed in column 2 of Table I by their structural formulas and will be referred to by the corresponding number in column 1. Many of the ethers could not be obtained in pure form and no attempt was made at purification. Ethylene glycol (1) was included in this study because it was a major impurity in (9). Ethanol, a common impurity in (10), was included for the comparison of this study with a previous investigation[1]. Small amounts of (13) and an impurity that is probably n-propyl alcohol were detected in (14).

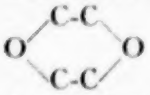
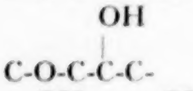
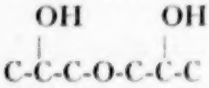
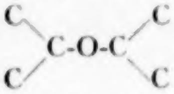
RESULTS

Elution variables

Fig. 1 represents the elution graphs for (1), (2) and (9) obtained by eluting the mixture through the various resins with a flow rate of 0.5 cm per minute of 2.0M ammo-

TABLE I

ELUTION DATA

No.	*Structural formula of ether*	*Values of C for ammonium sulfate eluents*					C_0	*k*
		0.01M	*1.0M*	*2.0M*	*3.0M*	*4.0M*		
1	HO-C-C-OH	1.32	1.60	1.96	2.37	2.98	1.32	0.085
2	HO-C-C-O-C-C-OH	1.37	2.11	3.40	5.30	8.84	1.33	0.205
3	C-O-C-C-OH	1.34	2.41	3.80	6.25	10.0	1.46	0.209
4		1.69	3.52	6.63	12.4	24.7	1.90	0.272
5	C-C-O-C-C-OH	1.41	2.86	5.83	11.5	23.7	1.44	0.303
6	 $\mathrm{C-O-C-\overset{OH}{\overset{\vert}{C}}-C-}$	1.37	2.81	5.72	11.3	24.5	1.38	0.318
7	 $\mathrm{C-\overset{OH}{\overset{\vert}{C}}-C-O-C-\overset{OH}{\overset{\vert}{C}}-C}$	1.32	3.10	6.81	15.8	37.7	1.33	0.358
8	C-O-C-C-O-C	1.36	3.36	7.10	16.1	38.9	1.41	0.357
9	C-C-O-C-C-O-C-C-OH	1.37	3.88	9.20	23.9	67.7	1.41	0.441
10	C-C-O-C-C	1.68	4.52	11.4	—	—	1.70	0.416
11	C-C-C-C-O-C-C-OH	2.50	7.28	20.9	—	—	2.50	0.461
12	C-C-O-C-C-O-C-C-O-C-C	1.54	6.24	23.0	—	—	1.70	0.560
13		2.04	6.96	—	—	—	2.04	0.52
14	C-C-C-O-C-C-C	3.14	12.1	—	—	—	3.14	0.59
15	C-C-C-C-O-C-C-O-C-C-C-C	5.33	—	—	—	—	5.33	—
16	C-C-C-C-O-C-C-C-C	6.90	—	—	—	—	6.90	—
—	C-C-OH	1.36	2.25	3.40	5.08	7.75	1.48	0.178

nium sulfate. The anion-exchange resins, Dowex 1-X4, and -X8, fail to separate (1) from (2). Dowex 50-X4 was chosen in preference to Dowex 50-X8 because the resin of lower cross-linkage is more porous to the large molecules encountered in this investigation.

The effect of flow rate, Fig. 2a, and sample size, Fig. 2b, are shown by elutions from Dowex 50-X4, 200-400 mesh, with 2.0*M* ammonium sulfate. The effects of these variables and the effect of resin mesh size are similar to those found earlier[1,3]. Ammonium sulfate solutions were also found to be suitable as eluents[1].

Distribution ratio and salting-out constants

For each elution performed, the distribution ratio *C* of the ether was calculated by means of the equation[6]

$$U^* = CV + V \quad \ldots\ldots\ldots \quad (1)$$

where U^* is the volume of effluent at the peak of the elution graph, measured in milliliters. The interstitial volume of the column *V* was determined to be 33.0% of the bed

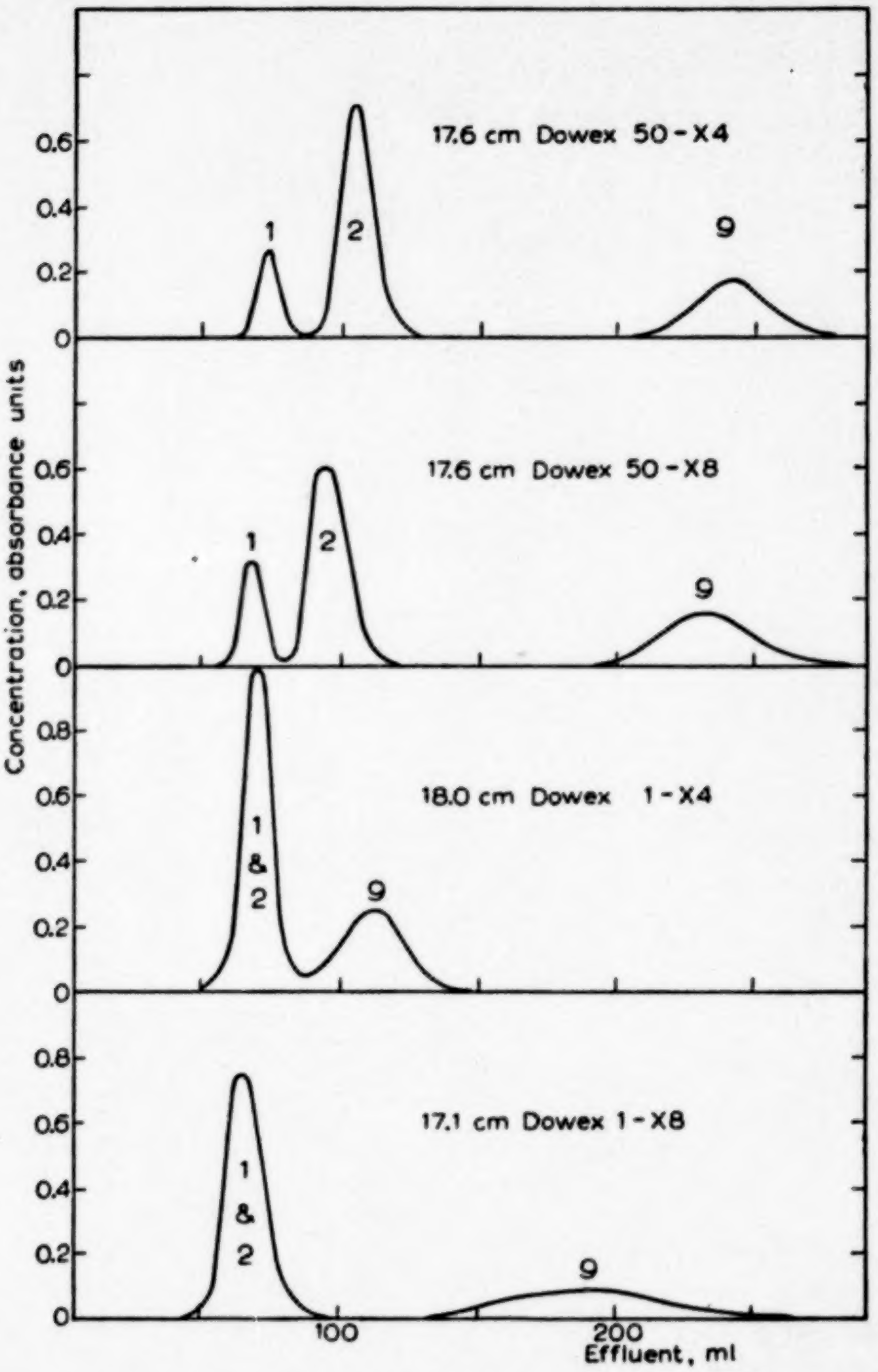


Fig. 1. Effect of resin and cross-linkage. Elution of (1), (2) and (9) on columns of cation- and anion-exchange resins of different cross-linkage. Each column had a cross-sectional area of 3.90 sq.cm.

volume for Dowex 50-X4, 200-400 mesh. Columns 3-7 in Table I list the values of C for various ammonium sulfate eluents. Plots of log C *vs.* M for several ethers are shown in Figs. 3 and 4. These straight lines follow the equation[1]

$$\log C = \log C_0 + kM \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Separation of mixtures

The data in Table I were used to calculate the conditions necessary[1] for the separation of synthetic mixtures which contained 0.05 mmol or less of each ether dissolved in 1

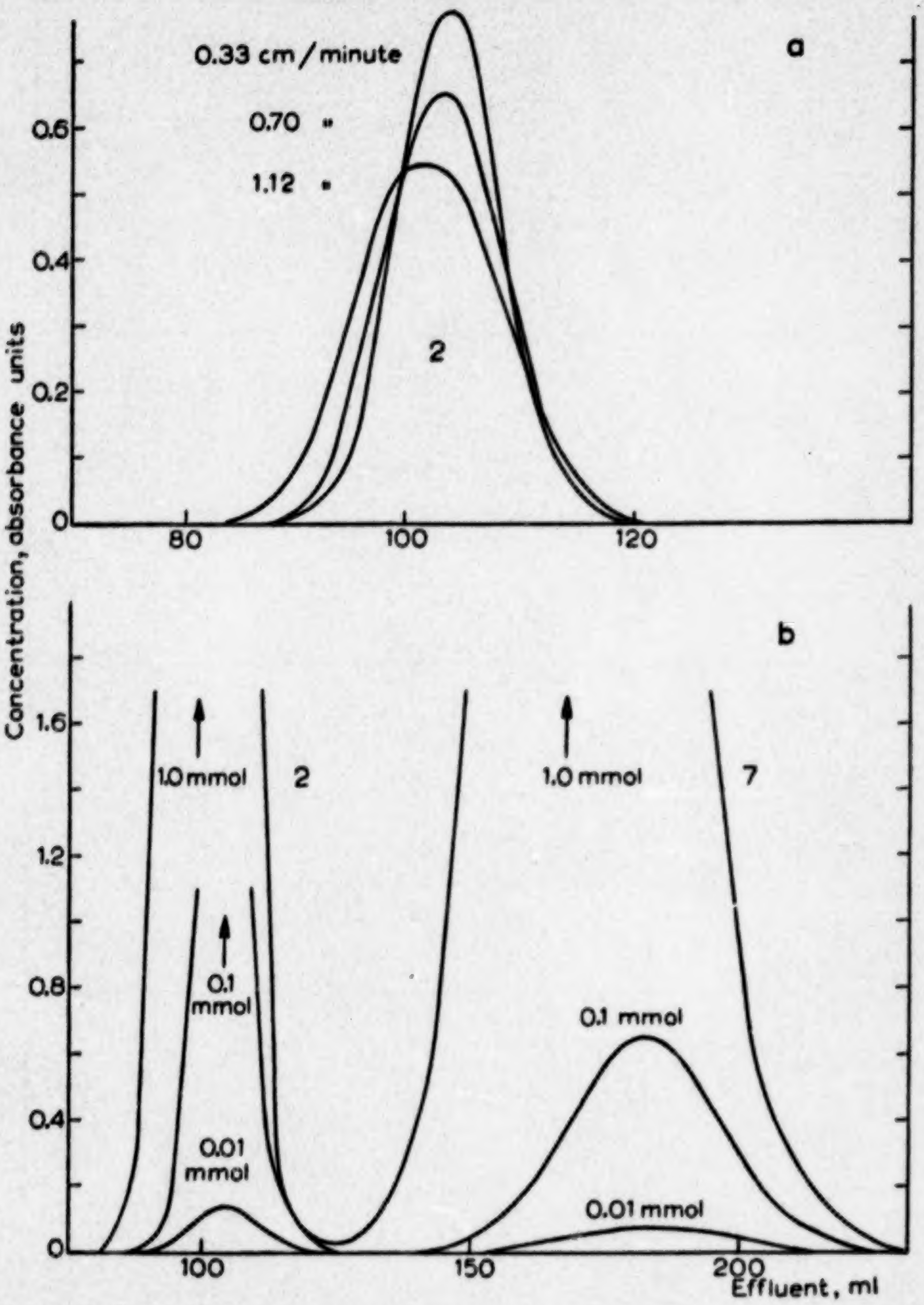


Fig. 2. The effect of various flow rates (a) and sample sizes (b) in salting-out chromatography. Dowex 50-X4, 200-400 mesh, 17.6 cm × 3.90 sq.cm.

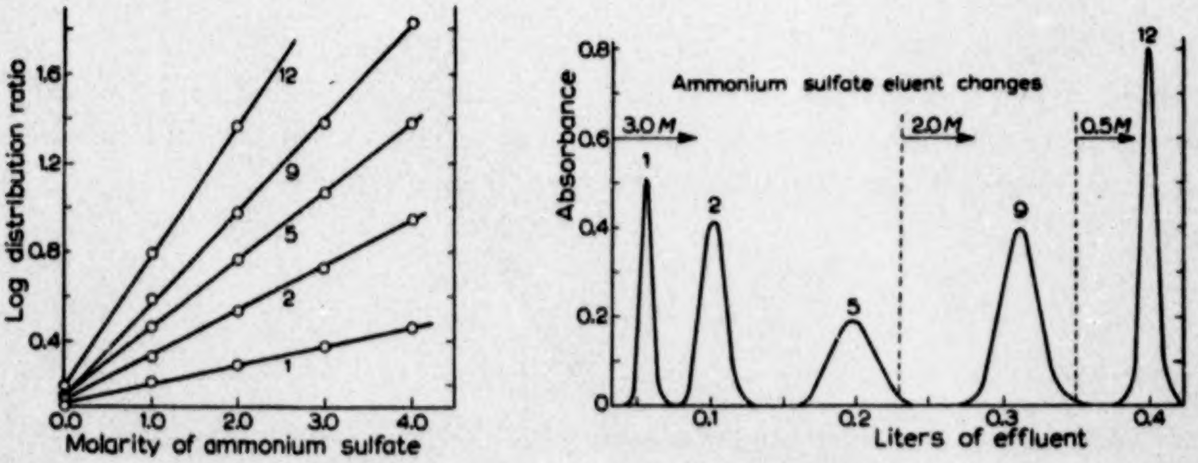


Fig. 3. Log C plots and the separation of a mixture of ethers on Dowex 50-X4, 200-400 mesh, 12.0 cm × 3.90 sq.cm, 0.7 cm per minute.

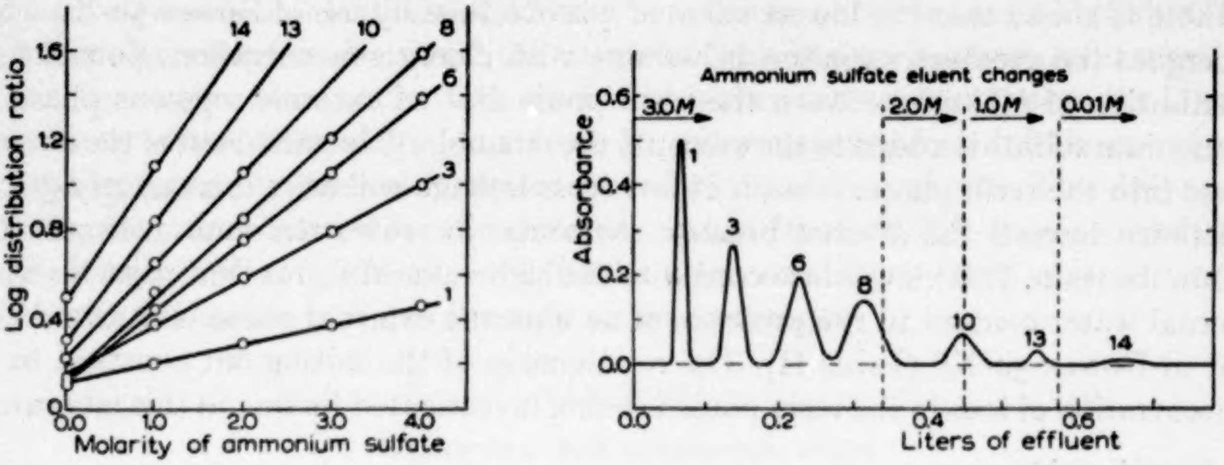


Fig. 4. Log C plots and the separation of a mixture of ethers on Dowex 50-X4, 200-400 mesh, 14.0 cm × 3.90 sq.cm, 0.7 cm per minute.

ml of water. For example, the values of U^* for the ethers separated in Fig. 3 on Dowex 50-X4, were calculated as 52.1, 99.4, 195, 311 and 406 ml. The observed values were 51.6, 97.9, 192, 306 and 394 ml. Fig. 4 illustrates the separation of another mixture of ethers under the same conditions.

DISCUSSION

Analysis

Quantitative analysis of complex ether mixtures is readily accomplished by the chromatographic procedure given above followed by oxidation with dichromate[4]. The hydroxy ethers have high reduction capacities in their reaction with dichromate in 50% sulfuric acid and therefore can be determined accurately in trace quantities. Some difficulty is likely to be encountered in the analysis of the simple aliphatic ethers. Low solubility in aqueous solution, low reduction capacities in the oxidation procedure and volatility combine to make the analysis difficult. Gas-liquid partition chromatography, although not as effective for the high-boiling hydroxy ethers, would probably be preferable for the separation of the volatile aliphatic ethers.

Theory

The extrapolated C_0 and the k value of equation 2 for each compound is given in the last two columns of Table I. Although straight lines were obtained with Dowex 50-X4, the slope k for ethanol has a lower value than the salting-out constants (k in Table II) obtained[1] with the higher cross-linked resins, Dowex 1-X8, and Dowex 50-X8.

TABLE II

COMPARISON OF ELUTION DATA OF ETHANOL WITH VARIOUS RESINS

Resin	C_0	C 4M $(NH_4)_2SO_4$	k	% Shrinkage 0.0 to 4.0M $(NH_4)_2SO_4$	g internal H_2O per g dry NH_4R	
					H_2O	4M $(NH_4)_2SO_4$
Dowex 50-X4	1.48	7.75	0.178	29.2	1.50	0.908
Dowex 50-X8	0.836	7.77	0.243	15.9	0.773	0.574
Dowex 1-X8	0.619	7.08	0.256	6.8	—	—

Table II shows that the lowest value of *k* is obtained by use of Dowex 50-X4 which undergoes the greatest variation in volume with eluent concentration. Consider the distribution of ethanol between the resin phase and an external aqueous phase. As ammonium sulfate is added to the mixture, the ethanol will be salted out of the external phase into the resin phase. A resin of low cross-linkage will offer increasingly greater resistance toward the alcohol because shrinkage increases the ionic concentration within the resin. This view is in accord with the high value of C_0 for Dowex 50-X4 whose internal water content in the presence of an aqueous external phase is nearly double that of Dowex 50-X8 (Table II). The relationship of the salting-out constant to the concentration of ions in the resin phase is being investigated further in this laboratory.

Carboxylic acids

Methods analogous to those used for the separation of the amines were employed in an attempt to separate carboxylic acids by salting-out chromatography. Solutions of tripotassium phosphate made excellent eluents because, by hydrolysis of the phosphate ion, the solutions were sufficiently basic to prevent ion formation by the amine. Similarly, it is necessary to use eluents that are sufficiently acidic to repress the ionization of the carboxylic acids if one is to avoid ion-exchange reactions on the resin. The ionization of propionic acid may be repressed to a negligible extent in 0.1*N* hydrochloric acid. A major difficulty arises at this point. Consider the addition of an anion exchanger (1) and a cation exchanger (2) to this mixture:

(1) Although propionic acid is virtually unionized in the external solution, upon entrance to the resin phase, it ionizes because the DONNAN membrane equilibrium[7] excludes hydrogen ions from the resin phase. Ionization is facilitated by the exchange of the propionate ion with the chloride form of the resin. The elution of a carboxylic acid from a column of Dowex 1 with 0.1*N* hydrochloric acid always produces an elution graph with two peaks when the effluent is analyzed for total acidity. The first peak, which immediately follows the interstitial volume of eluent, is due to the exchange reaction described above. The same is true also for other eluents used, *e.g.*, sodium or calcium chloride solutions which were 0.1*N* in hydrochloric acid.

(2) A cation exchanger in a form other than hydrogen would lead to ion-exchange reactions. Solutions of hydrochloric acid were therefore used for the elution of carboxylic acids from Dowex 50. Fractions of the effluent were analyzed by two methods: Fatty acids were extracted with chloroform and titrated with sodium hydroxide. Fruit acids and dicarboxylic acids were evaporated to dryness on a steam bath with subsequent titration. It was found that hydrochloric acid was poor as a salting-out agent and failed to give the large differences in the log *C* plots that are necessary for the separation of mixtures. Only slight improvement was found for sulfuric acid eluents. Linear log *C* plots were not obtained (for the fruit acids which could be analyzed by dichromate oxidation[4]) because of bisulfate formation in the eluent. The presence of sodium or calcium chloride in 0.1*N* hydrochloric acid and ammonium sulfate in sulfuric acid (the ratio of bisulfate to sulfate maintained constant at 0.1) increases the difference in *C* values, but in all cases, the separation of a mixture of carboxylic acids was not improved in comparison with the salt-free eluent because of an increased spread of the elution graphs.

Because of ion exchange, the distribution ratios were higher on the anion exchanger than on the cation exchanger especially for the more highly ionized carboxylic acids.

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The use of low concentrations of sodium or calcium chloride in 0.1*N* hydrochloric acid as eluent therefore decreased the values of *C* for the acids whose ionization constants were larger than 10^{-3}. With eluents of higher salt concentration, the *C* values increase by virtue of the salting-out effect. No advantage was found in the use of acidified eluents, again because of increased spread of the elution graphs. The elution data in Table III were obtained for the chloride form of Dowex 1-X8, 200-400 mesh, with an eluent of 0.1*N* hydrochloric acid. Under these conditions there is no salting-out effect and differences in *C* are due only to ion exchange.

TABLE III

VALUES OF *C* FOR CARBOXYLIC ACIDS

Lactic	1.45	Formic	2.19	Oxalic	5.70
Tartaric	2.09	Acetic	1.62	Malonic	4.86
Malic	2.57	Propionic	3.34	Succinic	4.67
Citric	3.92	*n*-Butyric	6.39	Glutaric	6.90
Fumaric	5.84	Isobutyric	12.4	Adipic	11.4
Maleic	7.90	*n*-Valeric	15.1		

The data show that the following mixtures may be separated: (1) acetic, formic, propionic, succinic, *n*-butyric and isobutyric acids; (2) lactic, malic, malonic, glutaric, and adipic acids.

ACKNOWLEDGEMENT

The authors express their gratitude to the Dow Chemical Company for generous financial support of this investigation.

SUMMARY

Distribution ratios of 15 ethers were determined with various ammonium sulfate eluents and were used to determine the conditions necessary for the separation of five- and seven-component mixtures by salting-out chromatography. The application of this technique was found to be less successful than ion-exchange chromatography for the separation of carboxylic acids.

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SALTING-OUT CHROMATOGRAPHY

IV. ALDEHYDES AND KETONES

by

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Ion-exchange chromatography has given rise to rapid quantitative separations of ionic substances[1] such as the alkali-metal[2], rare-earth[3] and halide ions[4]. An extension of this procedure, known as ion exclusion, has made possible the division of mixtures into an ionic fraction and a non-ionic fraction[5,6]. WHEATON AND BAUMAN[6] have demonstrated, qualitatively for the most part, the separation of non-ionic materials from each other using a water eluent. With the use of this approach, they have reasonably well separated sucrose, glycerine, triethylene glycol and phenol, as well as a number of two-component mixtures[6]. More recently, quantitative separations of multi-component mixtures of alcohols[7,8], amines[9], and ethers[10] have been effected in this laboratory by salting-out chromatography. In this procedure, the chromatographic separation of water-soluble non-electrolytes is performed with an ion-exchange resin as the stationary phase and aqueous salt solutions of varying concentrations as eluents.

The present paper reports the results of the application of salting-out chromatography to the separation of carbonyl compounds. Quantitative separations of many two-component aldehyde and/or ketone mixtures have been carried out by SJÖSTRÖM, GABRIELSON, AND SAMUELSON[11-14] with anion-exchange resins in the bisulphite form. In addition to this ion-exchange procedure, a few selected aldehydes and ketones have been separated by paper chromatography with filter-paper strips sprayed with a dilute solution of sodium bisulphite[15].

The results in the present paper are interpreted with the use of equation[16]

$$U^* = CV + V \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where U^* is the volume of effluent collected from the addition of the sample to the peak on the elution graph, C is the distribution ratio of the substance being eluted (quantity of the substance in the resin of any plate divided by the quantity in the interstitial volume of the same plate) and V is the interstitial volume of the column.

EXPERIMENTAL

Apparatus and reagents

The resins studied included two sulfonated polystyrenes (Dowex 50 and Amberlite CG 120) and two polystyrenes with quaternary nitrogen atoms (Dowex 1 and Amberlite CG 400). They were used in the ammonium and sulfate forms, respectively.

The details describing the preparation of the ion-exchange columns and the procedures for elutions have been described[8]. A glass-fiber disc was placed on top of each column to minimize disturbance of the resin bed during the addition of sample to the column. Fractions of approximately 6.0 ml were collected with an automatic fraction collector[16] and a siphon pipet calibrated for each eluent used. All absorbancy readings were taken on a Beckman Spectrophotometer, Model DU, with 10-cm cells. For pH measurements a Beckman pH meter, Model G, equipped with standard electrodes No. 290 and No. 270 was used.

Assayed reagent-grade salts were used in making up all eluents. All carbonyl compounds were of the best grade available. Acetone, methyl ethyl ketone and methyl propyl ketone were dried and redistilled. Propionaldehyde and butyraldehyde were purified by distillation. Acetaldehyde was prepared from paraldehyde and redistilled. Formaldehyde was prepared from para[illegible]rmaldehyde. A 0.5M stock solution was prepared[17] with hydroxylamine hydrochloride (Fischer H-330) recrystallized twice from ethanol. This solution is stable for at least two months, if it is stored in a refrigerator when not in use. This contrasts favorably with the 3-day stability period mentioned in the original reference[17]. A 0.1M solution of this reagent was prepared from the stock solution, as needed.

Analysis of effluent

Two methods were used to determine the concentration of the carbonyl compound in the effluent.

(1) In the determination of the distribution coefficients C of the individual compounds, the fractions were analyzed by a modification of the differential pH method of Roe and Mitchell[17]. Five milliliters of 0.1M hydroxylamine hydrochloride was added to each effluent fraction with stirring. After 5 minutes, the pH was determined. Unlike the original method, a different blank was determined for each eluent by measuring the pH of a mixture of the reagent and an effluent fraction containing no carbonyl compound. The quantity of carbonyl compound in each fraction was found by consulting a calibration graph of ΔpH *vs.* the amount of carbonyl compound.

(2) The foregoing method is not applicable to the determination of carbonyl compounds in fractions of uncertain concentrations of eluent salt, such as are encountered when the concentration of eluent is changed during an elution. In these cases, the carbonyl compound was analyzed by mixing the fraction of effluent with 5 ml of 0.1N sodium dichromate in concentrated sulfuric acid, diluting with 25 ml of water and measuring the absorbance of the resulting Cr(III)[18].

Interstitial volumes

The void volumes were determined by the method previously reported[10].

RESULTS

Sample size, flow rate, particle size and cross-linking

An extensive series of preliminary elutions of acetone, 2,3-pentanedione and cyclohexanone was performed in order to find the best conditions for separations. The elutions, performed on 3.90-sq. cm columns of Dowex 1 with 1M ammonium sulfate as eluent, gave the following results: (1) Flow rates of 0.20, 0.25, 0.40 and 0.80 cm per minute produced no significant change in any of the elution graphs. (2) From the studies of sample size, it was concluded that no more than 0.050 to 0.100 mmol of each compound should be taken. Quantities greater than this cause a shift to the left of both U^* and the leading edge of the elution graph. This shift is most noticeable with compounds of high C value. (3) The degree of separation and the sharpness of the elution graphs were increased as the mesh size was changed from 50-100 to 100-200 to 200-400. (4) Elutions from columns of Dowex 1-X2, 1-X4, 1-X8 and 1-X10 gave both an increase in selectivity and a broadening of the elution graphs with increasing cross-linkage. The 4% and 8% nominal cross-linkings were selected for more detailed studies.

Choice of eluent

Ammonium sulfate solutions were found to be satisfactory eluents.

Interstitial volumes

Values of the interstitial volumes for the 200-400 mesh resins used were found to be: Dowex 50-X4, Lot No. 4101-7, 0.34 V_B; Dowex 50-X8, Lot No. 4034-20, 0.37 V_B;

Dowex 1-X4, Lot No. 1241, 0.40 V_B; Dowex 1-X8, Lot No. 4054-41, 0.41 V_B; Amberlite CG 120, Lot No. 8147, 0.45 V_B and Amberlite CG 400, Lot No. 8011, 0.59 V_B. V_B denotes the bed volume. These are the average values of 2 to 4 determinations. Microscopic examination of the Amberlite resins showed that they were very irregularly shaped in contrast with the spherical nature of the Dowex resin particles. This irregularity in shape is probably the cause of the high V values found for these resins.

Although we have found the interstitial volumes of the Dow resins to be very nearly the same from batch to batch, we would not expect this to be true of the Amberlite resins because of this irregularity in particle shape. The maximum flow rates obtainable were lower with the Amberlite resins.

TABLE I

VALUES OF DISTRIBUTION RATIO C

No.	Carbonyl compound	Molarity of ammonium sulfate					
		0.00	0.50	1.0	1.5	2.0	3.0
I Dowex 50-X4							
1	Acetone	1.53	—	2.89	3.84	5.17	10.0
2	Methyl ethyl ketone	1.89	—	4.43	6.50	9.71	22.8
3	Methyl propyl ketone	2.55	—	6.89	11.11	18.9	—
II Dowex 50-X8							
1	Acetone	1.01	—	2.15	3.16	4.47	8.60
2	Methyl ethyl ketone	1.41	—	3.60	5.64	8.73	—
3	Methyl propyl ketone	1.96	—	5.98	10.3	17.5	—
III Amberlite CG 120							
1	Acetone	1.05	1.47	2.14	2.80	3.94	8.28
2	Methyl ethyl ketone	1.42	2.18	3.28	4.74	7.24	19.4
3	Methyl propyl ketone	1.95	3.10	4.93	8.62	14.5	—
IV Amberlite C6 400							
1	Acetone	0.34	0.49	0.75	1.09	1.43	3.67
2	Methyl ethyl ketone	0.73	1.05	1.97	2.77	4.52	—
3	Methyl propyl ketone	1.49	2.55	4.16	—	—	—

TABLE II

VALUES OF DISTRIBUTION RATIO C
(Dowex 1-X4, 200–400 mesh)

No.	Carbonyl compound	Molarity of ammonium sulfate					
		0.00	0.50	1.00	2.00	3.00	4.00
1	Acetone	0.57	1.02	1.32	2.58	4.56	8.07
2	Acetoin	0.55	1.06	1.39	2.58	4.24	7.33
3	Diacetyl	0.85	1.46	1.89	3.45	5.69	12.3
4	2,5-Hexanedione	0.73	1.41	2.17	5.15	13.3	30.8
5	Diacetone alcohol	0.61	1.30	2.04	5.85	12.7	—
6	Methyl ethyl ketone	0.83	1.60	2.41	5.10	12.3	24.0
7	Cyclopentanone	1.09	1.96	2.95	6.24	13.9	30.8
8	2,3-Pentanedione	1.26	2.49	3.28	7.28	14.3	—
9	2,4-Pentanedione	1.24	2.20	3.30	7.18	14.8	—
10	Methyl isopropyl ketone	1.24	2.42	3.88	10.1	27.6	—
11	Methyl propyl ketone	1.39	2.77	4.32	11.5	32.2	—
12	Diethyl ketone	1.27	2.70	4.32	11.3	33.0	—
13	Cyclohexanone	1.67	3.09	4.89	12.7	—	—

Distribution ratios and salting-out constants

Acetone, methyl ethyl ketone and methyl propyl ketone were eluted from columns of the six resins employed in this study with various concentrations of ammonium sulfate. The distribution ratios were calculated with equation (1) from the data of the various elutions. Table I lists the values of C for four different resins. Table II contains the distribution ratios for thirteen ketones on Dowex 1-X4. Table III summarizes the C values for thirteen ketones and four aldehydes on Dowex 1-X8.

The logarithms of these values were plotted against the molarity of ammonium sulfate. These plots followed the equation[8]

$$\log C = \log C_0 + kM \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

TABLE III

VALUES OF DISTRIBUTION RATIO C

(Dowex 1-X8, 200–400 mesh)

No.	*Carbonyl compound*	*Molarity of ammonium sulfate*					
		0.00	*0.50*	*1.00*	*2.00*	*3.00*	*4.00*
1	Formaldehyde	1.05	0.93	1.00	0.98	0.97	0.88
2	Acetaldehyde	0.80	0.98	1.22	1.52	2.18	2.92
3	Acetone	0.70	0.93	1.53	3.00	6.12	10.9
4	Acetoin	0.76	0.96	1.38	2.91	6.13	10.8
5	Diacetyl	1.25	2.06	2.20	4.60	8.50	13.9
6	2,5-Hexanedione	1.06	1.47	2.56	6.87	22.4	—
7	Diacetone alcohol	0.78	1.36	2.31	7.31	22.5	—
8	Propionaldehyde	1.37	1.86	2.50	4.58	7.70	—
9	Methyl ethyl ketone	1.28	2.00	3.02	8.21	21.1	—
10	Cyclopentanone	1.70	2.59	4.01	8.83	—	—
11	2,3-Pentanedione	1.92	2.59	4.49	12.8	—	—
12	2,4-Pentanedione	1.90	2.73	4.34	12.9	21.8	—
13	Methyl isopropyl ketone	2.12	3.59	5.76	16.5	—	—
14	Butyraldehyde	2.82	4.42	5.81	—	—	—
15	Methyl propyl ketone	2.51	4.56	7.52	19.6	—	—
16	Diethyl ketone	2.52	4.42	7.16	19.6	—	—
17	Cyclohexanone	3.09	5.17	8.61	—	—	—

where C_0 is the distribution ratio in pure water, k is the salting-out constant and M is the molarity of the salt solution. These constants for three compounds and six resins are given in Table IV, along with C value ratios between methyl propyl ketone and acetone. Salting-out parameters for the other carbonyl compounds on Dowex 1-X4 and Dowex 1-X8 are given in Table V.

Separation of carbonyl mixtures

The data in Table III and plots of log C *vs.* M were used to select the conditions necessary for the separation of mixtures containing 0.05 to 0.10 mmol of each carbonyl compound dissolved in 1 ml of water. Equation (1) was used to calculate U^* for compounds eluted with a single eluent. FREILING[19] has derived equations which enable one to calculate U^* for both discontinously and continuously graded eluents. When his equations are translated into our symbolism they become:

TABLE IV

SALTING-OUT CONSTANTS ($(NH_4)_2SO_4$)

$$\log C = \log C_0 + kM$$

No.	Resin	Carbonyl compound						$\frac{C\ \text{methyl propyl ketone}}{C\ \text{acetone}}$	
		Acetone		*Methyl ethyl ketone*		*Methyl propyl ketone*			
		log C_0	*k*	*log* C_0	*k*	*log* C_0	*k*	H_2O	2.0*M* $(NH_4)_2SO_4$
1	Dowex 1-X4, 200-400	—0.175	0.283	0.000	0.360	0.180	0.440	2.44	4.46
2	Dowex 1-X8, 200-400	—0.160	0.318	0.105	0.397	0.410	0.448	3.58	6.53
3	Dowex 50-X4, 200-400	0.183	0.272	0.282	0.358	0.345	0.429	1.67	3.66
4	Dowex 50-X8, 200-400	0.015	0.314	0.150	0.398	0.295	0.476	1.94	3.91
5	Amberlite CG 120	0.000	0.307	0.155	0.363	0.278	0.436	1.86	3.69
6	Amberlite CG 400	—0.465	0.330	—0.140	0.390	0.173	0.448	4.39	8.20

TABLE V

No.	Compounds	Dowex 1-X4		Dowex 1-X8	
		log C_o	k	log C_o	k
1	Formaldehyde	—	—	0.009	—0.013
2	Acetaldehyde	—	—	—0.095	0.142
3	Acetoin	—0.098	0.244	—0.160	0.302
4	Propionaldehyde	—	—	0.140	0.255
5	Diacetyl	0.020	0.260	0.090	0.270
6	2,5-Hexanedione	—0.001	0.350	—0.065	0.467
7	Diacetone alcohol	—0.082	0.400	—0.102	0.472
8	Cyclopentanone	0.130	0.332	0.230	0.365
9	2,4-Pentanedione	0.182	0.294	0.270	0.373
10	2,3-Pentanedione	0.182	0.294	0.270	0.383
11	Butyraldehyde	—	—	0.462	0.309
12	Methyl isopropyl ketone	0.220	0.423	0.310	0.450
13	Diethyl ketone	0.220	0.423	0.410	0.448
14	Cyclohexanone	0.290	0.455	0.488	0.460

(1) For *two eluents*

$$U^* = V + U_1 + C_2 \left(V - \frac{U_1}{C_1}\right) \quad \ldots\ldots\ldots\ldots (3)$$

(2) For *three eluents*

$$U^* = V + U_1 + U_2 + C_3 \left(V - \frac{U_1}{C_1} - \frac{U_2}{C_2}\right) \quad \ldots\ldots (4)$$

(3) For $n + 1$ *eluents*

$$U^* = V + \Sigma\, U_n + C_{n+1} \left(V - \Sigma \frac{U_n}{C_n}\right) \quad \ldots\ldots\ldots (5)$$

In the above equations, U_1, U_2, ... U_n correspond to the actual number of milliliters of each eluent used. Equations (2) and (3) give results differing from those previously published from this laboratory[20,8] by less than the experimental error.

The following separations were carried out on the sulfate form of Dowex 1-X8, 200-400 mesh: (1) A nearly quantitative separation of a mixture of the first four members of the homologous series of saturated aliphatic aldehydes and the corresponding plot of log C *vs.* M is shown in Fig. 1. The calculated values of U^* were 53, 100 184 and 261 ml as contrasted with the observed values of 57, 105, 185 and 262 ml.

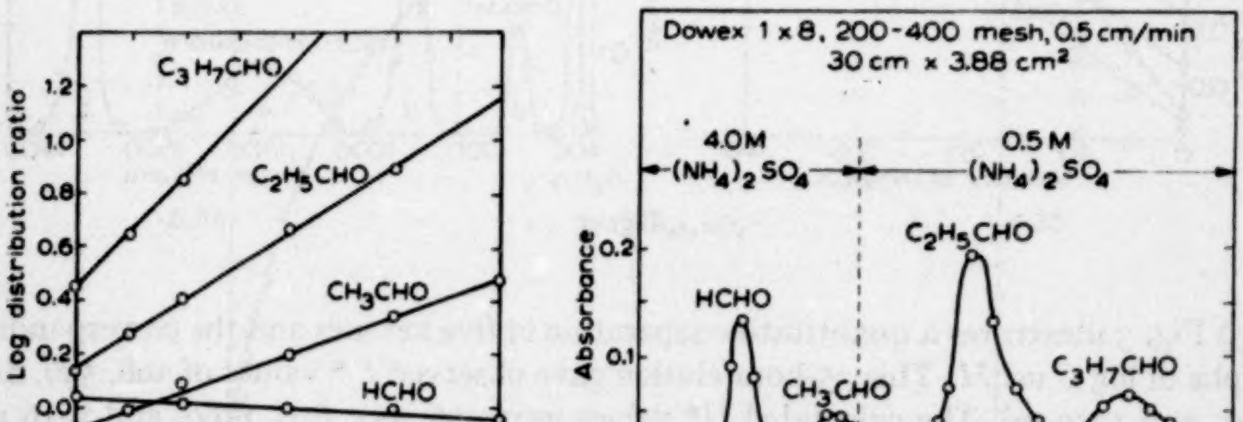

Fig. 1

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This separation requires only three hours. Quantitative separation of the last two compounds can be accomplished by the use of a 40-cm column or an eluent change to $0.5M$ at 150 ml or an eluent change to $1.0M$ at 120 ml followed by a change to water at about 225 ml.

(2) The separation of a mixture of four ketones and the corresponding plot of log C against M is shown in Fig. 2. The elution and analysis required 10 hours. The calculated values of U^* were 208, 371, 524 and 696 ml; observed values were 205, 386, 556 and 718 ml. The separation could be improved by increasing the column height or by using $0.5M$ or $1.0M$ ammonium sulfate as the final eluent.

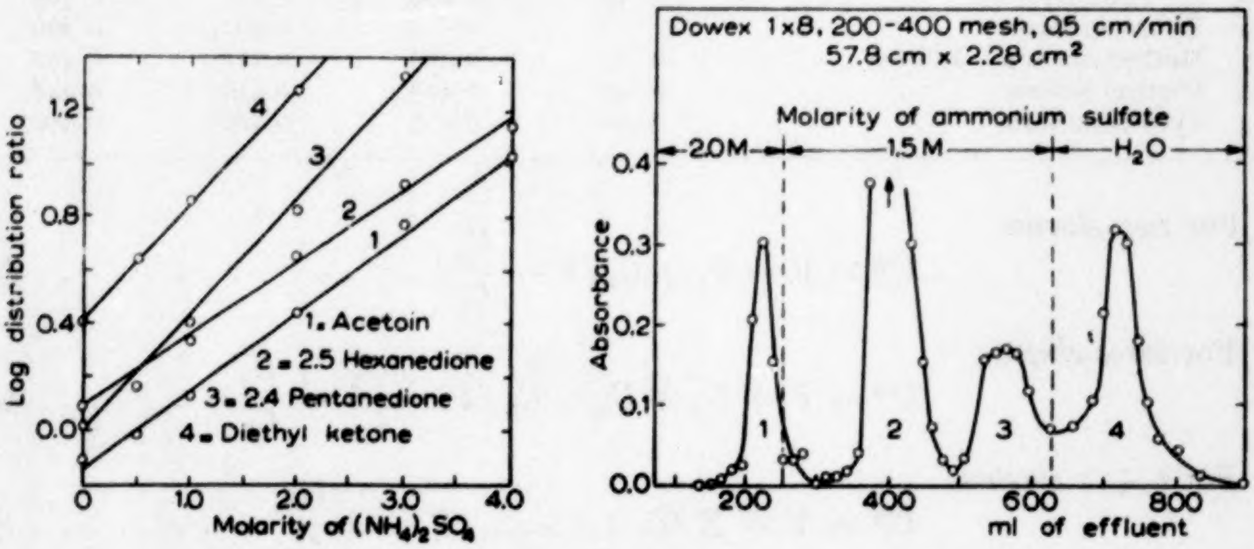


Fig. 2

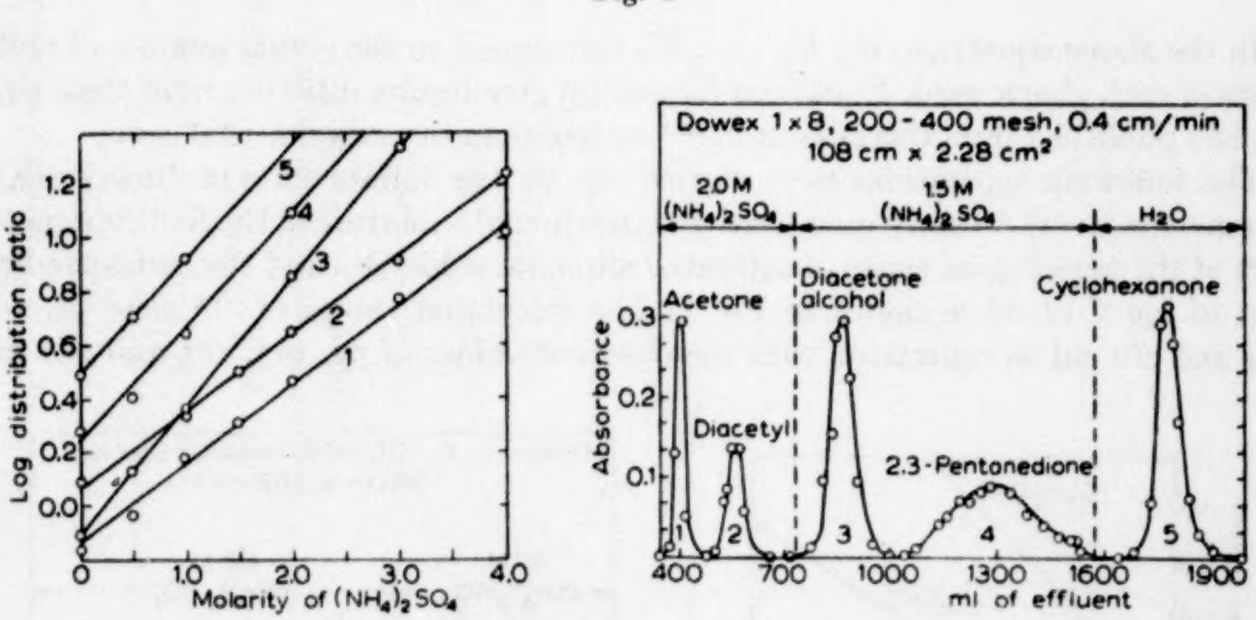
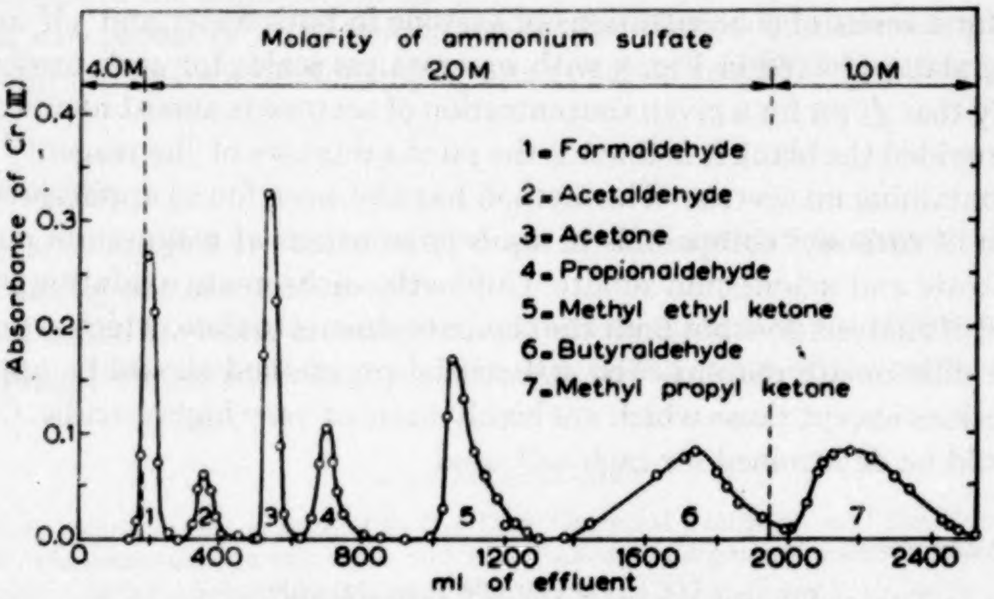


Fig. 3

(3) Fig. 3 illustrates a quantitative separation of five ketones and the corresponding graphs of log C *vs.* M. This 35-hour elution gave observed U^* values of 396, 556, 849, 1262, and 1750 ml. The calculated U^* values were 396, 554, 820, 1160, and 1716 ml. Extrapolated C values were used for the last two calculations.

(4) It was of interest to try to obtain a separation of a mixture containing the lower straight chain homologs of both the aldehydes and ketones. Fig. 4 illustrates the results

obtained. The observed U^* values of 193, 351, 535, 697, 1086, 1741 and 2150 ml checked very well with the calculated values of 193, 344, 540, 704, 1096, 1800 and 2145 ml. The elution required 65 hours.



Dowex 1 x 8, 200 - 400 mesh, 110 cm x 2.28 cm², 0.35 cm/min .

Fig. 4

DISCUSSION

Determination of carbonyl compounds in the effluent

Roe and Mitchell[17] have shown that carbonyl compounds can be determined in methanol, ethanol, benzene and water by measuring the decrease in pH which occurs,

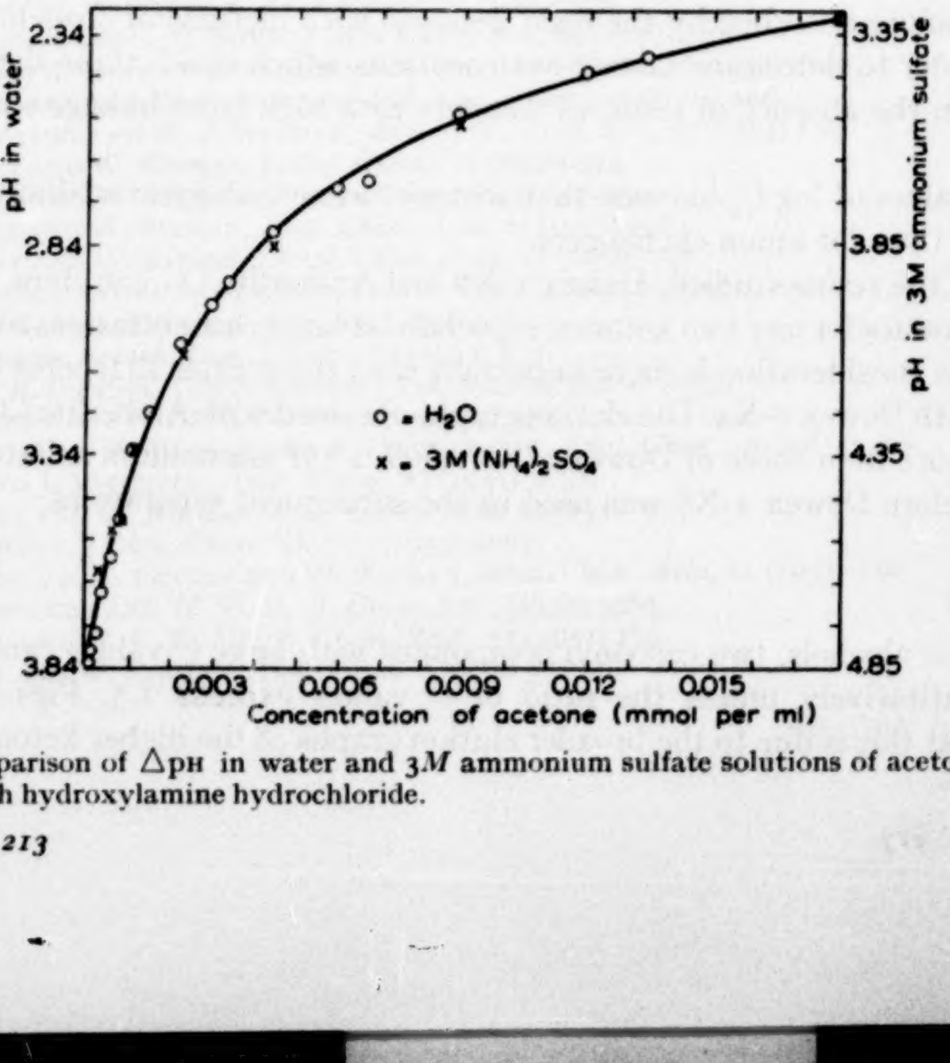


Fig. 5. A comparison of ΔpH in water and $3M$ ammonium sulfate solutions of acetone following oximation with hydroxylamine hydrochloride.

when the unknown carbonyl solution is added to an aqueous solution of hydroxylamine hydrochloride. Regardless of the solvent used, the final pH values were the same for a given carbonyl solution. When carbonyl compounds dissolved in $3M$ ammonium sulfate solution were added to the reagent the pH decreased for high concentrations and increased for low concentrations. An extensive quantitative investigation of $\triangle$ pH was made for a series of concentrations of acetone in both water and $3M$ ammonium sulfate. The data, plotted in Fig. 5 with separate pH scales for each medium, prove conclusively that $\triangle$ pH for a given concentration of acetone is almost identical for each medium, provided the blank is defined as the pH of a mixture of the reagent[17] and 10 ml of eluent containing no acetone. The method has also been found applicable in the determination of carbonyl compounds in aqueous solutions of magnesium nitrate, ammonium nitrate and magnesium sulfate. Unlike the dichromate oxidation procedure[8], this method of analysis does not limit the choice of eluents to those which are unreactive toward the dichromate reagent. The differential pH method should be applicable to all salt solutions except those which are highly basic or very highly acidic. Calibration curves should be determined for each salt used.

Salting-out constants

The data in Tables IV and V reveal the following facts:

(1) Values of k for any one solute are not quite as constant as those for the alcohols[8]. However, the k values of the alcohols were determined only with resins of 8% cross-linking whereas the k values of the ketones were determined with resins of 4 and 8% cross-linkage. The constants for resins with the same cross-linkage agree closely. All the compounds studied exhibit lower salting-out constants with the resins of 4% cross-linkage. These facts are due to the greater shrinkage of the lower cross-linked resin with increasing salt concentration in the external solution and the attendent decrease of the internal water content[10]. REICHENBERG AND WALL[21] have shown that with each solute, at a given molarity in the outside solution, the amounts of both water and solute absorbed by the resin decrease with increase of cross-linking of the resin. In order to determine salting-out constants which check those determined by methods[22] in the absence of resin, exchangers with high cross-linkage should be employed.

(2) The values of log C_0 indicate that acetone has a much greater affinity for cation exchangers than for anion exchangers.

(3) Of all the resins studied, Dowex 1-X8 and Amberlite CG 400 show the greatest ratios of C values for any two ketones, especially at large concentrations of ammonium sulfate. This consideration is more important than the greater sharpness of the peaks obtained with Dowex 1-X4. The elution graphs obtained with Amberlite CG 400 spread 50-100% more than those of Dowex 1-X8, when a $1M$ ammonium sulfate eluent was used. Therefore Dowex 1-X8 was used in the subsequent separations.

Separations

Unlike the alcohols, two carbonyl compounds with large C values cannot be separated quantitatively unless the ratio of C values exceeds 1.5. Figs. 2, 3 and 4 indicate that this is due to the broader elution graphs of the higher ketones and aldehydes.

The log C plots of Fig. 3 indicate the difficulty of separating 2,5-hexanedione from acetoin and 2,4-pentanedione. At large concentrations of ammonium sulfate the C values of 2,5-hexanedione and acetoin converge. On the other hand, convergence of the log C plots of 2,4-pentanedione and 2,5-hexanedione occur at low concentrations.

The inclusion of the higher homologs of the aldehydes and/or ketones in the scheme of analysis can probably be accomplished by the elution of these compounds with aqueous solutions of such solubilizing agents as acetic acid[8,23], ethanol or propanol.

Work in progress

More detailed studies are being carried out by the authors in connection with the theory of salting-out chromatography.

Variables which are being investigated include the nature of the eluent salt, and the capacity, ionic form, cross-linkage and the functional group of the resin.

ACKNOWLEDGEMENT

The authors express their gratitude to the Dow Chemical Company and the Rohm and Haas Company for the resins used in this work, to Dr. R. SARGENT for general advice and to the National Science Foundation for a fellowship for one of the authors (A.B.).

SUMMARY

Mixtures of aldehydes and/or ketones have been separated by salting-out chromatography. The effects of such variables as sample size, flow rate, concentration of the eluent, cross-linking, mesh size, and type of resin on the elution behavior of the compounds were studied. Salting-out parameters were determined for thirteen ketones and four aldehydes. The differential pH method of ROE AND MITCHELL is applicable to the determination of carbonyl compounds in aqueous salt solutions.

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SOLUBILIZATION CHROMATOGRAPHY

I. PHENOLS AND ALCOHOLS

by

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In a recent[1,2] study of the salting-out chromatography of alcohols of low molecular weight, it was found that excessively large volumes of water are needed to elute *n*-amyl alcohol from the column of ion-exchange resin but that 1.0 *M* acetic acid removes this alcohol readily. This suggested the possibility of separating mixtures of phenols and higher alcohols by chromatography through ion-exchange resins with aqueous solutions of acetic acid as eluents. The designation "solubilization chromatography" is suggested for this method.

In the interpretation of the results, use is made of the equation[3]

$$U^* = CV + V \quad \text{. . . . .} \quad (1)$$

where U^* is the volume of effluent collected from the point of addition of the sample, to the peak of the elution graph, and C is the distribution ratio of the phenol or alcohol (the total quantity of alcohol in the resin of any given plate divided by the quantity in the solution of the same plate). The interstitial volume of the column is represented by V.

EXPERIMENTAL

Materials

All phenols and alcohols used in this study were of the best grade available. No further purification was required.

Since weak-acid and weak-base resins were found to be unsatisfactory for the salting-out chromatography of the lower alcohols[2], only the strong-acid cation-exchange resin, Dowex 50, in the hydrogen form, and the strong-base anion-exchange resin, Dowex 1, in the acetate form, were used in this study. For a similar reason, only resins of 200-400 mesh were used. The resins were packed in the columns as previously described[2].

The ratio of the interstitial volume to the bed volume, V/V_B, was determined for each resin used[4], and found to be: 0.368 for Dowex 50-X8, lot No. 4034-20; 0.344 for Dowex 50-X4, lot No. 4101-7; 0.407 for Dowex 1-X8, lot No. 4054-41; 0.402 for Dowex 1-X4, lot No. 1241.

Eluents were prepared by dilution of reagent-grade glacial acetic acid.

Elutions

The samples were introduced upon the resin bed as previously reported[2]. A maximum of 0.2 mmole of sample, dissolved in 1.0 ml of at least 50% acetic acid, was eluted with a flow rate of 0.4 to 0.5 cm per minute, unless otherwise specified. Fractions of approximately 6.0 ml were automatically collected with the aid of a constant-volume collecting device[3].

Analysis

The fractions were analyzed by mixing them with 5.0 ml of 0.02 *M* sodium dichromate in concentrated sulfuric acid, diluting with 25 ml of distilled water, and measuring spectrophotometrically the resultant Cr(III)[5].

Solubility studies

Excess quantities of *n*-amyl and *n*-hexyl alcohols were shaken with solutions of 0 to 6 *M* acetic acid. The relative quantity of alcohol dissolving in the aqueous phase in each case was determined by oxidation of an aliquot with dichromate solution[5].

RESULTS AND DISCUSSION

Sample solutions

Most of the compounds used in this study have only slight solubilities in water. Rather than introduce the samples into the column as suspensions in water, 0.02*M* solutions were prepared in 50% to 80% acetic acid.

In order to determine the effect of this small amount of acetic acid on the value of U^*, four elutions of 0.020 mmole of isoamyl alcohol from Dowex 50-X8 (16.4 cm × 3.9 cm²) were performed with water as the eluent. All experimental conditions were constant except that the samples were dissolved in one ml of water, 50% ethanol, 50% acetic acid, and 80% acetic acid. The observed values of U^* were 109, 106, 106, and 107 ml, respectively. The differences are within experimental error. Isoamyl alcohol was used so that a 0.02*M* solution in water could be prepared.

Choice of eluent

Acetic acid was chosen because it readily dissolves the organic compounds studied, and because it is one of the few organic compounds which is not oxidized by dichromate in the analytical procedure used.

Cross-linking

The effect of cross-linking was studied by eluting a mixture of *n*-amyl, *n*-hexyl, and *n*-heptyl alcohols with 1.0*M* acetic acid from columns containing 17.5 cm of Dowex 1-X4 and Dowex 1-X8, and 17.0 cm of Dowex 50-X2, 50-X4, and 50-X8 (Fig. 1).

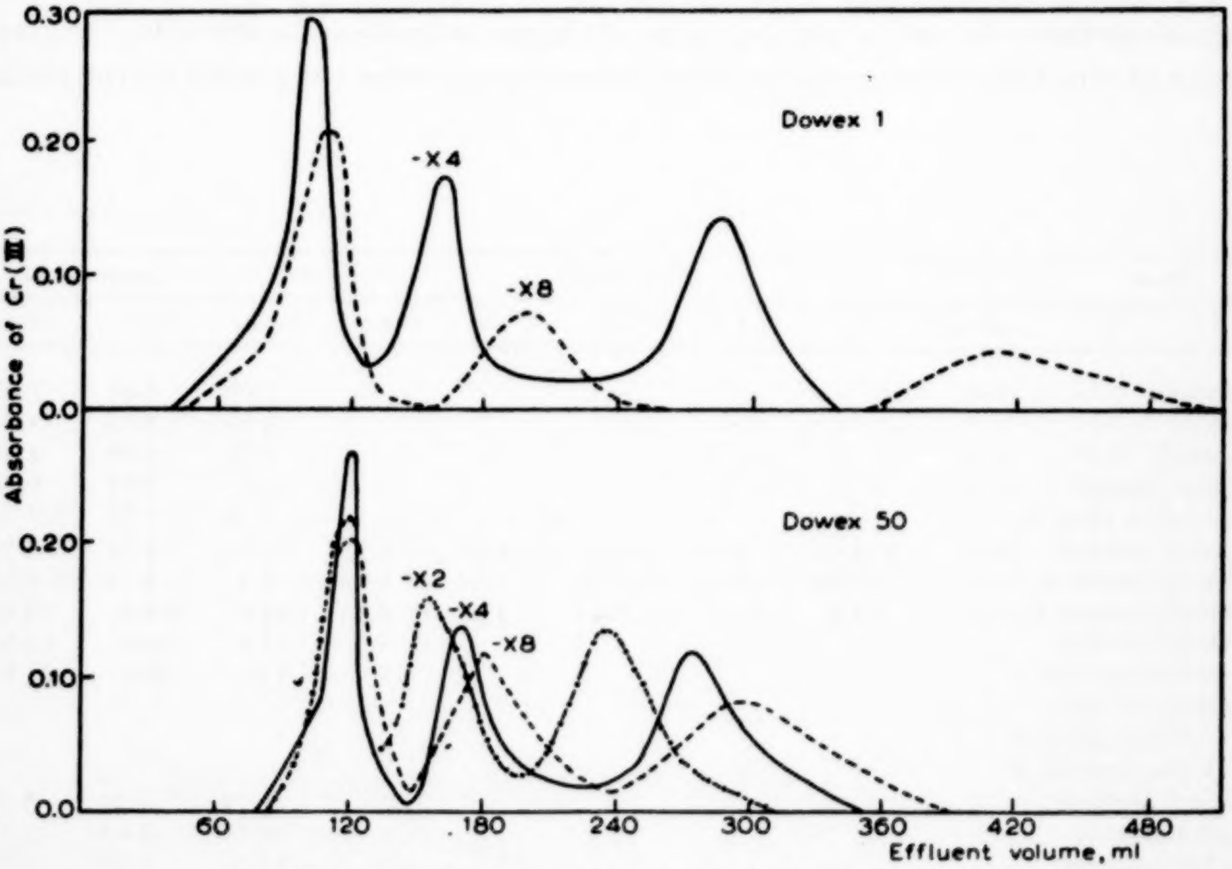

Fig. 1. Crosslinkage study (% divinylbenzene).

Dowex 50 was chosen for the separations because it sorbs the higher alcohols less strongly than does Dowex 1, and it was expected that the separation could be extended to longer-chain compounds in this way. There is little difference between Dowex 50-X4 and 50-X8 in regard to selectivity and shape of elution graphs. Dowex 50-X8 was chosen because of its greater dimensional stability.

Flow rate

The effects of flow rate was studied by eluting *n*-heptyl alcohol from Dowex 1-X8 (17.7 cm × 3.9 cm^2) with 6.0*M* acetic acid at 0.15, 0.30, 0.40, and 0.50 cm per minute. There is negligible effect on the U^* for the indicated changes in flow rate.

Distribution ratios and plots of log C vs. molarity of acetic acid

Tables I and II list, respectively, the distribution ratios, *C*, as calculated by equation (1), for the phenols and alcohols on Dowex 50 and Dowex 1, and the results of plotting log *C vs.* molarity of acetic acid for the various compounds and resins studied. Fig. 2 shows the plots of log *C vs. M* for the alcohols on Dowex 50-X8, and Fig. 3 presents similar graphs for the phenols on Dowex 1-X8. These data indicate the following:

1. Although *tert.*-amyl and *n*-amyl alcohols are absorbed by Dowex 50 more than by Dowex 1, the reverse is true of *n*-octyl and *n*-nonyl alcohols. The force of attraction between a resin and alcohol may be considered to be the sum of the attraction between the hydrocarbon portions of the resin and alcohol and the attraction between the ions of the resin and hydroxyl group of the alcohol. It is to be expected that Dowex 1 with its greater number of carbon atoms per functional group, would be a better absorbant for the higher alcohols than Dowex 50.

2. Contrary to the results of salting-out chromatography[2], some of the plots of log *C vs. M* are linear for only a limited region. At large molarities of acetic acid, the graphs for the alcohols tend to curve downward and converge, while the graphs for the phenols

TABLE

VALUES

Resin		*Dowex 50-X4*					*Dowex 50-X8*			
	[HAc]	*0.0*	*1.0*	*2.0*	*4.0*	*6.0*	*0.0*	*1.0*	*2.0*	*4.0*
Catechol							3.06	2.41	1.96	1.4
Phenol							4.66	3.65	3.03	2.0
o-Cresol							7.85	5.66	4.38	2.5
o-Nitrophenol							12.8	8.67	6.46	2.9
tert.-Amyl alcohol							2.19	1.86		
n-Amyl alcohol		4.97	4.22	3.51	2.51	1.77	4.61	3.85	3.30	2.2
n-Hexyl alcohol		8.60	6.44	5.34	3.32	1.85	7.97	6.12	4.88	2.8
n-Heptyl alcohol		16.4	11.0	8.44	4.45	1.85	14.9	10.8	8.28	3.8
n-Octyl alcohol							27.5	20.7	13.8	5.3
n-Nonyl alcohol							55.1	36.7	21.6	7.4
n-Decyl alcohol										9.6
n-Undecyl alcohol										
n-Dodecyl alcohol										
Benzyl alcohol							5.71	4.30	3.76	2.5
Cyclohexanol							4.80	4.04	3.58	2.5
o-Chlorophenol							13.5	8.48	6.80	3.7

on Dowex 1-X8 show curvature upward and divergence in some cases. The authors are unable to explain these results.

3. The graphs for the phenols on Dowex 1-X8 are concave upward when $M < 1$. This is probably due to ion exchange. Only at these small concentrations of acetic acid is there appreciable ionization of the phenols. Then the phenolate ions undergo ion exchange with the acetate ions of the resin. The facts that the phenol graphs are linear, in this region, on the cation-exchange resin and that the graphs of the alcohols are linear, in this region, on both resins support this point of view.

4. The slopes obtained for a given alcohol from the straight portions of the graphs did not check from resin to resin as in salting-out chromatography[2]. This is not sur-

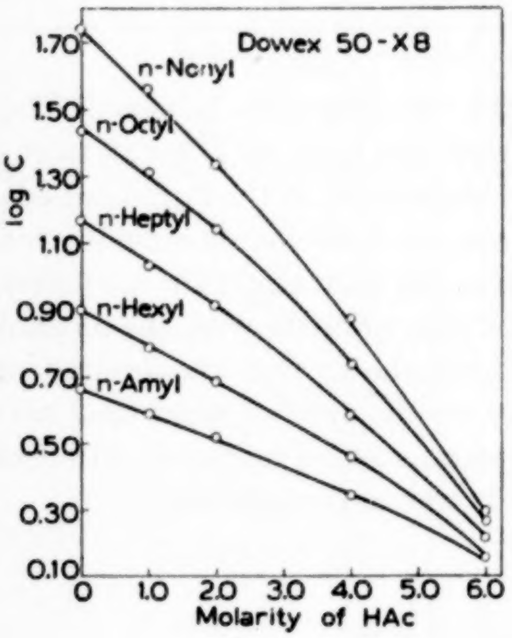

Fig. 2.

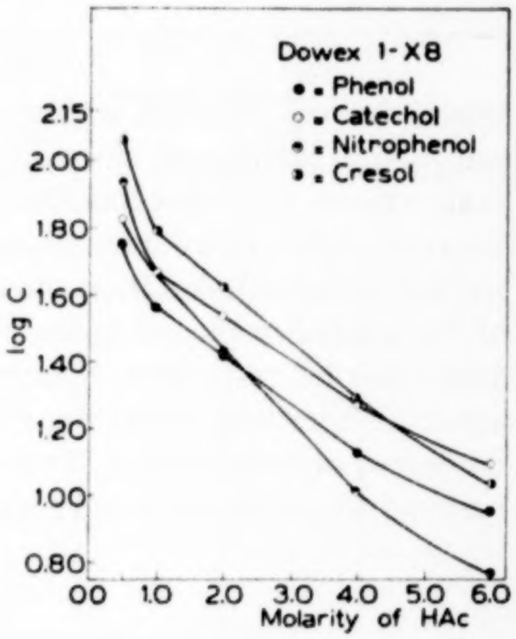

Fig. 3.

ISTRIBUTION RATIO, *C*

	Dowex 1-X4					*Dowex 1-X8*					
6.0	*0.0*	*1.0*	*2.0*	*4.0*	*6.0*	*0.0*	*0.5*	*1.0*	*2.0*	*4.0*	*6.0*
0.994							67.1	46.5	34.5	18.9	12.4
1.39							56.1	36.5	26.8	13.6	9.02
1.57							115.9	61.2	42.1	19.9	10.9
1.76							86.1	46.2	26.1	10.4	5.84
	1.18	1.18	1.12	0.998	0.754						
1.43	2.97	2.58	2.36	1.93	1.41	3.64		2.91	2.29	1.50	1.02
1.46	5.39	4.78	4.04	2.83	1.67	8.38		6.17	4.40	2.38	1.36
1.65	10.7	9.37	7.70	5.59	2.17	20.3		14.1	9.79	4.12	2.12
1.85	25.4	20.4	16.1	9.99	3.10						
1.98	63.6	48.2	37.7	22.7	4.19						
2.69					5.31						
3.55											
4.77											
1.55											
1.67											
2.03											

TABLE II

Resin	*Dowex 50-X4*		*Dowex 50-X8*		*Dowex 1-X4*		*Dowex 1-X8*	
	Negative slope	*Extent of linearity*	*Negative slope*	*Extent of linearity*	*Negative slope*	*Extent of linearity*	*Negative slope*	*Extent of linearity*
Catechol			0.082	0-6*M*			0.131	1-4*M*
Phenol			0.088	0-6*M*			0.143	1-4*M*
o-Cresol			0.115	0-6*M*			0.163	1-4*M*
o-Nitrophenol			0.148	0-6*M*			0.216	1-4*M*
tert.-Amyl alcohol			0.072	0-6*M*	0.020	0-4*M*		
n-Amyl alcohol	0.075	0-6*M*	0.080	0-4*M*	0.051	0-6*M*	0.095	0-6*M*
n-Hexyl alcohol	0.106	0-4*M*	0.112	0-4*M*	0.072	0-4*M*	0.137	0-6*M*
n-Heptyl alcohol	0.139	0-4*M*	0.128	0-2*M*	0.072	0-4*M*	0.164	0-6*M*
n-Octyl alcohol			0.155	0-2*M*	0.103	0-4*M*		
n-Nonyl alcohol			0.203	0-2*M*	0.110	0-4*M*		

prising because there is an important difference in the two processes involved. The salt used in salting-out chromatography is excluded from the resin by Donnan membrane effects. Its major function is to make the alcohol less soluble in the liquid outside the resin phase. In solubilization chromatography, the acetic acid eluents are not ionic enough to be excluded from the resin, and they therefore not only affect the solubility of the alcohol or phenol in the interstitial volume, but also compete with the alcohol and water for resin sites. REICHENBERG AND WALL[6] have shown that the amount of acetic acid getting inside the resin depends markedly on the type of resin used and its degree of cross-linking. This means that the four resins studied represent different systems whose results should not be expected to check among themselves.

TABLE III

SOLUBILITIES IN SOLUTIONS OF ACETIC ACID

(Arbitrary units of absorbance)

[HAc]	*0.0*	*1.0*	*2.0*	*4.0*	*6.0*	*Negative slope*
n-Amyl alcohol	0.476	0.515	0.543	0.693	1.28	0.033
n-Hexyl alcohol	0.248	0.280	0.325	0.457	0.663	0.065

In Table III, the solubilities of two alcohols in various solutions of acetic acid are given. Plots of the negative logarithm of the solubility *vs.* concentration of acetic acid give straight lines from 0 to 2*M* acetic acid; then they curve downward like the graphs of Fig. 2. The slopes of the linear portions did not check any of the slopes obtained for these two alcohols on any of the four resins used.

SEPARATION OF MIXTURES

Figs. 4 and 5 show the separations obtained for mixtures of four phenols and six aliphatic alcohols, respectively, and the conditions and eluent changes used. By use of the data in Table I, the concentration and position of eluent changes were calculated prior to the separations by a method reported previously[7,8]. In order to separate the first members of the mixtures, the elutions were begun with 1.0*M* acetic acid. The

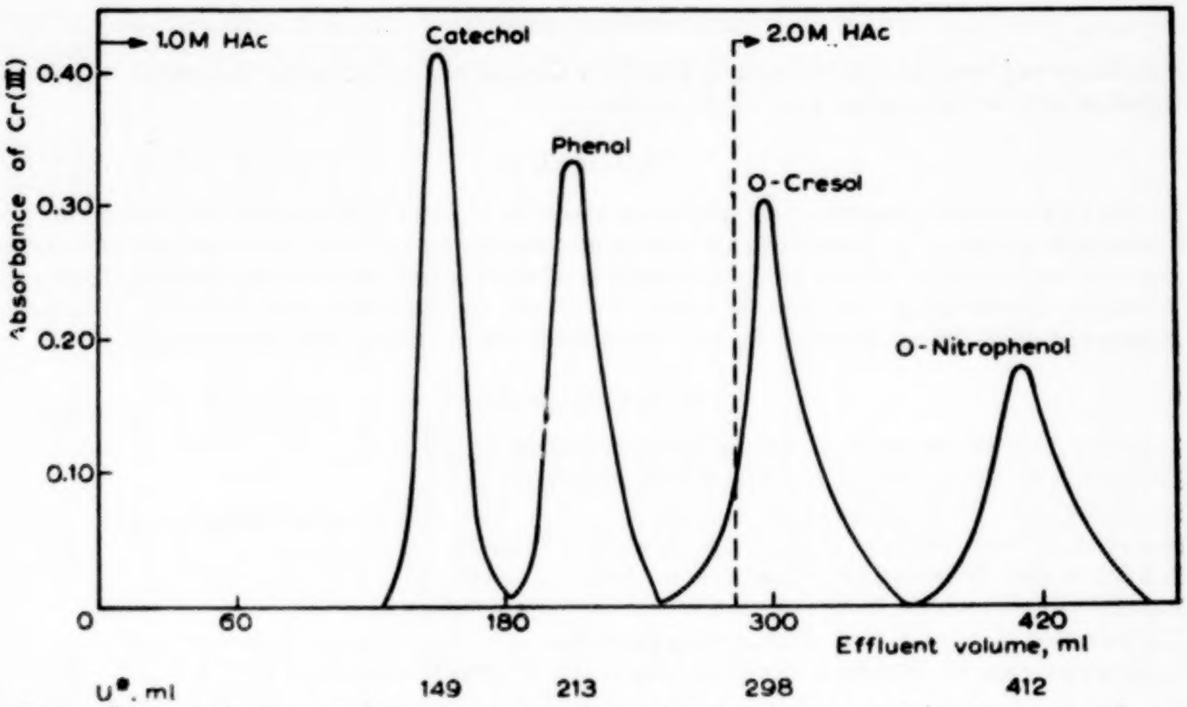

Fig. 4. Separation on Dowex 50-X8, 200-400 mesh, hydrogen form, 51.6 cm × 2.28 cm², 0.45 cm per min.

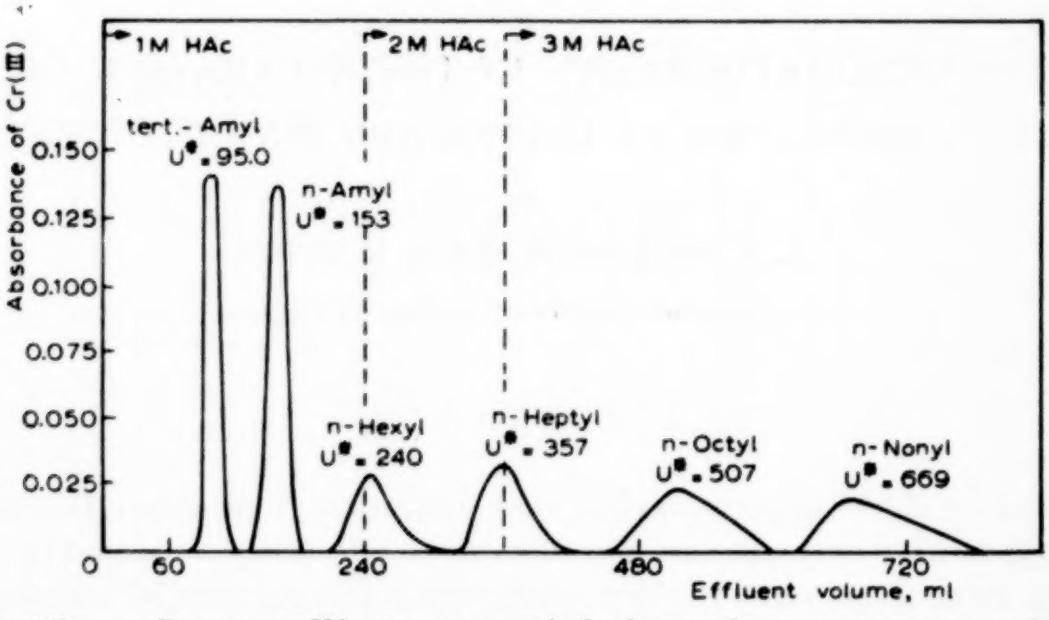

Fig. 5. Separation on Dowex 50-X8, 200-400 mesh, hydrogen form, 39.0 cm × 2.28 cm², 0.45 cm per min.

concentration of eluent was then raised as quickly as possible so as to obtain both separation and rapid elution of the remaining components of the mixtures. The calculated positions of the peaks for the phenols were 148, 201, 288, and 395 ml; values for the alcohols were 94, 159, 233, 361, 536, and 648 ml.

Benzyl alcohol, cyclohexanol, and *o*-chlorophenol were not included in the phenol separation shown. Under the given conditions, *o*-chlorophenol would have U^* identical to *o*-nitrophenol; cyclohexanol would have U^* close to phenol; benzyl alcohol would be eluted between phenol and *o*-cresol, but the three would not be separated.

Extension of the alcohol separation beyond nonyl alcohol was attempted on Dowex 50-X8, -X4, and -X2, but failed in each case because of the severe spreading of the longer-chain alcohols.

ACKNOWLEDGEMENT

The authors express their gratitude to the Dow Chemical Company for financial support of this investigation and for the resins used in the work.

SUMMARY

Mixtures of four phenols and of six aliphatic alcohols (C_5 to C_9) have been separated by solubilization chromatography, a procedure in which the mixture is eluted from an ion-exchange resin with aqueous solutions of acetic acid. The effects of such variables as cross-linking, flow rate, and concentration of eluent on the elution behavior of the compounds were studied, and the results were compared with those obtained for the lower alcohols in salting-out chromatography.

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ELECTRO-CHROMATOGRAPHY IN THE SEPARATION OF IONS.

PART IV. SEPARATION OF COPPER AND TIN GROUP METALS

by

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MAJUMDAR *et al.*[1,2,3], in their previous communications, have shown that the cations in a binary, ternary or quaternary mixture can be effectively separated by Durrum's technique, using some common electrolytes, which also function as complex-forming agents. Thus they have been able to separate from each other ions of the platinum metals including gold and some members of the sulphide group.

This paper records the ionic movements of the cations of the copper group (Hg^{+2}, Pb^{+2}, Bi^{+3}, Cu^{+2}, Cd^{+2}) and tin group (As^{+3}, Sb^{+3}, Sn^{+2}) and the migration sequences of the ions of the copper group when present in a three-, four- or five-component mixture, and those of the tin group in a binary mixture. All the ions of the copper group are separated from a five-component mixture with a decinormal solution of potassium chloride as the electrolyte at a working voltage of 150 V for 5 hours.

It may be mentioned that LEDERER AND WARD[4] report the separation of the members of the copper group with hydrochloric acid as the electrolyte. We find, however, that with the said electrolyte, Cd and Pb form slightly overlapping zones and while ammonium or sodium chloride behave like hydrochloric acid, potassium chloride acts differently and is better suited for the separation of ions of the copper group. While working in this laboratory, MUKHERJEE[5] in collaboration with the senior author found

TABLE I

EFFECT OF ELECTROLYTES (0.1N) ON IONIC MOVEMENTS IN cm

Ions	*HNO_3*	*H_3PO_4*	*$HClO_4$*	*HCl*	*NH_4Cl*	*NaCl*	*KCl*	*NaBr*	*NH_4 oxalate*	*KI*	*Acetic acid*	*Tartaric acid*	*Citric acid*	*Oxalic acid*	*Na K tartrate*	*Na citrate*
Hg^{+2}	−3.7	−1.0	−0.7	+5.4	+5.9	+6.0	+6.4	+9.0	0.0	+7.8	0.0	0.0	0.0	−0.6	+0.3	+0.4
Pb^{+2}	−3.2	0.0	−6.8	−3.6	−3.2	−3.5	−3.6	−0.6	0.0	0.0	−4.9	−4.8	−4.7	0.0	+1.0	+3.5
Bi^{+3}	−3.0	0.0	−1.7	+2.6	0.0	0.0	0.0	0.0	+3.5	+0.7	−0.6	+1.0	+1.3	0.0	+4.1	+7.1
Cu^{+2}	−5.8	−8.6	−7.0	−4.3	−6.8	−6.2	−8.0	−3.1	+3.5	−0.5	−1.5	−2.7	−3.4	0.0	+3.5	+8.1
Cd^{+2}	−3.8	−7.9	−5.7	−3.3	−3.0	−2.9	−3.0	−3.1	0.0	+3.0	−0.6	−9.8	−9.6	0.0	+0.4	+1.5
As^{+3}	0.0	−1.4	−1.4	−0.3	−0.4	−0.9	−0.6	0.0	−0.4	−0.7	−0.7	0.0	+0.6	−0.5	0.0	0.0
Sb^{+3}	−0.6	0.0	−0.5	0.0	−0.4	0.0	0.0	−0.2	+5.1	0.0	0.0	−0.4	+0.8	0.0	+2.5	+5.6
Sn^{+2}	−2.0	0.0	−0.5	−2.0	−0.5	−0.6	−0.9	−0.4	+5.6	+1.5	−0.9	−1.5	0.0	+3.0	+3.0	+5.9

Ions	*$(NH_4)_2CO_3$*	*NH_4CNS*	*KCN(aq.)*	*KCN (pH 6.0)*	*EDTA(aq.)*	*EDTA (pH 4.8)*	*EDTA (0.1N NH_4OH)*	*Thiourea (aq.)*	*Thiourea (pH 5.8)*	*Thiourea (0.1N HCl)*
Hg^{+2}	0.0	+5.1	+11.3	+1.0	+6.5	+4.1	+3.7	0.0	−3.0	−2.5
Pb^{+2}	0.0	−3.0	0.0	0.0	+6.0	+4.1	+2.5	0.0	−1.4	−3.2
Bi^{+3}	0.0	0.0	0.0	0.0	+2.5	+2.4	+2.6	−0.9	+0.5	+1.7
Cu^{+2}	0.0	0.0	+12.0	+1.3	+6.0	+4.8	+3.3	−1.6	−2.0	−1.0
Cd^{+2}	−2.5	−6.0	+8.6	−0.5	+6.1	+4.0	+2.8	0.0	−1.4	−1.7
As^{+3}	−2.6	0.0	0.0	0.0	−0.9	0.0	+0.5	−1.2	−1.4	−1.4
Sb^{+3}	−0.8	0.0	0.0	0.0	+1.4	+2.0	0.0	−0.4	−0.3	−0.3
Sn^{+2}	0.0	−0.3	0.0	0.0	−0.5	+2.0	+0.5	−0.7	−1.1	−1.4

TABLE II

MIGRATION SEQUENCES OF IONS PRESENT IN MIXTURES

Electrolyte (0.1N)	*Migration sequence*
HNO_3	: As, Sn—; : Sb, Sn—
H_3PO_4	: Bi, Hg, Cu—; : Bi, Hg, Cd— : Pb, Hg, Cd—; : Pb, Hg, Cu—; : Sn, As—
$HClO_4$	: Hg, Bi, Cd, Pb—; : Hg, Bi, [Cd, Cu]—
HCl	+ Hg, Bi : [Cd, Pb], Cu— : As, Sn—; : Sb, Sn—
NH_4Cl	+ Hg: Bi[Cd, Pb, Cu]—
NaCl	+ Hg: Bi[Cd, Pb], Cu—
KCl	+ Hg: Bi, Cd, Pb, Cu—
NaBr	+ Hg: Bi, Cu—; + Hg: Bi, Cd—
KI	+ Hg, Cd: Cu—; + Hg, Cd: Pb—; + Hg, Cd, Bi:; + Sn: As—; + Sn, Sb:
Acetic acid	: Sb, Sn—
Tartaric acid	: Hg, Pb, Cd—; : Hg, Cu, Cd—; + Bi: Cu, Cd—; + Bi: Pb, Cd—
Citric acid	: Hg, Pb, Cd—; : Hg, Cu, Cd—; + Bi: Cu, Cd—; + Bi: Pb, Cd—
Oxalic acid	+ Sn: As—; + Sn, Sb:
NH_4 oxalate	+ Sb: As—; + Sn: As—
Na citrate	+ Bi, Pb, Hg:; + Bi, Pb, Cd:; + Cu, Pb, Cd:; + Cu, Pb, Hg:; + Sb, As:; + Sn, As:
Na K tartrate	+ Sn, As:; + Sb, As:
NH_4CNS	+ Hg: Bi, Cd—; + Hg: Bi, Pb—; + Hg: Cu, Pb—; + Hg: Cu, Cd—
KCN(aq.)	+ Cu, Cd, Pb:; + Cu, Cd, Bi:; + Hg, Cd, Bi;: + Hg, Cd, Pb:
$(NH_4)_2CO_3$	: Sb, As—; : Sn, As—
EDTA(aq.)	+ Sb: As—
EDTA (pH 4.8)	+ Sb, As:

that the separation of the ions of the tin group was possible when a 0.5*N* sodium citrate solution was used as the electrolyte; we, however, could not confirm his observations and observed, on the other hand, that antimony and tin formed overlapping zones.

EXPERIMENTAL

The experimental technique was the same as reported in earlier papers[1,2,3], using nearly the same common electrolytes and of the same strength, that is 0.1*N*. Ionic migration was effected at a potential of about 150 V maintained for 5 hours.

A mixture of solutions containing the nitrates of the cations of the copper group and a mixture of solutions containing the chlorides of the tin group were used separately in the form of a small drop (0.01 ml) containing about 15 μg of each ion.

Table I reports the ionic movements of the ions of the copper and tin groups. From the migration values, although a large number of separations appeared to be possible for mixtures of ions of each group taken separately, only a few as recorded in Table II with migration sequences could be achieved; the other ions invariably formed diffused overlapping bands owing perhaps to some sort of influence exerted by one ion on another, thus checking each other's rate of movement.

DISCUSSION

The ionic movements are obtained by measuring the distance from the centre of the original spot to the centre of the electro-chromatogram. A movement of the ion towards the anode is represented by a + sign, the same towards the cathode by a — sign and the starting point is shown by the symbol :. The square brackets indicate that the enclosed cations have a portion of their migration zone in common.

Mercuric ion behaves almost in the same way as the mercurous ion, as reported in Part III of this series[3], *i.e.* mostly as the anionic complex. Bismuth is more or less similar to mercuric ion in most of the electrolytes; in a few, where it is precipitated, its movement is restricted. Copper and cadmium ions behave as anionic complexes in sodium citrate, Na K tartrate, KCN(aq.) and EDTA; and with KI, cadmium and mercury from stable anionic complexes.

Tin group ions show very feeble movement and are cationic in most cases. Arsenic is anionic only in presence of citric acid and EDTA (0.1*N* NH_4OH), while the same anionic character is exhibited by antimony and tin in presence of Na K tartrate, EDTA (pH 4.8), sodium citrate and ammonium oxalate. Stable anionic complexes of tin with potassium iodide and oxalic acid have been helpful for the separation of tin from antimony or arsenic. In spite of the best attempts, the three ions of this group could not be separated in any of the mentioned electrolytes.

The difference in migration values of the ions caused by the change of pH in thiourea and EDTA can only be explained as being due to the differences in the stability of the complexes.

SUMMARY

The ionic migration and hence the migration sequences of the ions of the copper and the tin groups have been determined in a number of common electrolytes which act as complexing agents. Separation of several three-, four- and five-component mixtures of copper group elements has been effected. Of the electrolytes, hydrochloric acid, sodium chloride and potassium chloride, the last gives the best and most complete separation of all the copper group ions from a mixture, a potential of 150 V being maintained for 5 h. The metals of the tin group cannot be separated completely from each other under the experimental conditions; only separation from binary mixtures is possible.

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ELECTRO-CHROMATOGRAPHY IN THE SEPARATION OF IONS

PART V. SEPARATION OF THIRD GROUP METALS

by

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MAJUMDAR AND SINGH[1,2] in their previous communications have shown how, by a suitable choice of the electrolyte, several binary, ternary, and quaternary mixtures of the cations of the silver, copper, and tin groups can be effectively separated. A complete separation of the cations of the silver group can be effected by potassium chloride or cyanide as an electrolyte and the copper group ions only by the use of potassium chloride solution.

This paper records the migration sequences of the ions of the third analytical group (Be^{+2}, Fe^{+3}, Cr^{+3}, Al^{+3}, Ti^{+4}, Zr^{+4}, Th^{+4}, UO_2^{+2}) present in a mixture. Owing perhaps to the same degree of stability of the complexes formed, few separations have been achieved, and not more than four ions in a mixture can be separated under the experimental conditions since the migration zones are closer to each other.

EXPERIMENTAL

The solutions of the ions, Be^{+2}, Fe^{+3}, Cr^{+3}, Al^{+3}, Ti^{+4}, Zr^{+4}, Th^{+4} and UO_2^{+2}, were prepared from their nitrates, except in the case of titanium, which was taken as the chloride, owing to its degree of hydrolysis being less. About 0.01 ml of a ternary or a quaternary mixture containing 15 μg of each ion was used as a test solution. The electrolytes used were more or less the same as reported in an earlier paper[1] and the strength of the electrolytes was 0.1 *N*. Experimental technique followed was identical to that reported in the previous papers (*loc. cit.*) with a working time of 5 hours and a potential of 150 V. Table I reports the migration sequences of ions from their mixtures.

TABLE I

MIGRATION SEQUENCES OF IONS PRESENT IN MIXTURES

Electrolytes (0.1N)	*Sequences of separation*
HCl	:Zr, Ti -; :Zr, (Fe,Al) -; :Zr,(Fe,Cr) -; :Zr, (U, Fe) -; :Zr, (Th, Cr) -
NH_4Cl	:Ti, U, Be -; :Zr, U, Be -; :Th, U, Be -; :U, Al, Be -
KCl	:Zr, Th, U, Al -; :Zr, Th, U, Be - ;Ti, (Th, U), Be -; :Ti, (Th, U), Al -
HNO_3	:Th, Zr -; :Zr, Ti -; :Cr, (U, Zr) -
NH_4NO_3	:Zr, U, Be -; :Ti, U, Be - :Ti, Th, Be -; :Zr, (Th, U), Be -
CH_3COONH_4	:Al, Be -; :Cr, Al -; :Fe, Al -; +U : Th, Be -; +U : Zr, Al -; +U : (Th, Al) -; +U : Zr, Be -
KI	:U, Al, Fe -; :Ti, (Al, Fe) -; :Zr, Al, Fe -
$Na_2S_2O_3$	+U : Zr, Al, Fe -; +U : (Th, Al), Fe-; :Ti, Al, Fe -
NH_4CNS	:Zr, U, (Al, Be) -; :Zr, Th, (Al, Be) -; :Th, U, Be -
NaOH or Na_2CO_3	+ Al, X:

X = mixture of Be, Ti, Zr, Th, U, Fe and Cr. For explanation of symbols, see text.

DISCUSSION

In Table I the migration of the ions towards the anode is shown by a + sign, the starting by the symbol: and the migration towards the cathode is indicated by a — sign. The ions within the brackets show that they have a slight common migration zone although they are well detected individually.

In general the migration of the ions of the third group is considerably low and all the ions move towards the anode in presence of NaK tartrate and Na citrate.

Ferric ion shows two bands with electrolytes such as H_2SO_4, CH_3CO_2H, Na citrate, NH_4CNS, and is mostly cationic. Because of the anionic character of aluminium in alkali it is possible to separate it from all the other ions present in a mixture. Beryllium ion shows a faster rate of movement, less degree of complex formation, and in a few instances abnormal spreading of the zone.

Of the other members of this group, Ti^{+4}, Zr^{+4}, Th^{+4} and UO_2^{+2}, the first three show practically the same behaviour in having slower movement, while uranium in the anionic form exhibits considerable movement in presence of ammonium hydroxide and ammonium carbonate.

SUMMARY

The ionic migration and migration sequences of the ions of group III, Fe^{+3}, Cr^{+3}, Al^{+3}, Be^{+2}, Ti^{+4}, Zr^{+4}, Th^{+4}, UO_2^{+2}, have been determined in a number of common electrolytes. Owing to their similar behaviour towards ionic migration, besides separations from their binary and ternary mixtures, only a few separations from quaternary mixtures as Zr-Th-U-Be, Zr-Th-U-Al, Zr-Th-Al-Be, Zr-U-Al-Be, Ti-Th-U-Be, Ti-Th-U-Al, U-Zr-Al-Fe and U-Th-Al-Fe are possible.

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SÉPARATION DES ALCALINO-TERREUX PAR CHROMATOGRAPHIE SUR COLONNE DE CELLULOSE

par

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INTRODUCTION

Dans une publication antérieure[1] nous avons décrit une méthode chromatographique de séparation sur cellulose de doses traceuses de radiobaryum et de radiostrontium à l'aide du mélange méthanol-éther-HCl 12*N* (75-25-5: v/v) et nous avons eu l'occasion d'appliquer avec succès la technique à la séparation de ^{140}Ba et ^{89}Sr „carrier free" extraits d'un échantillon de nitrate d'urane irradié aux neutrons.

Il nous a paru intéressant d'étudier la possibilité de l'emploi de ces éluants à base de méthanol pour séparer les autres alcalino-terreux; Ca-Sr et Ba-Ra[2,3,4,5].

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DÉTAILS EXPÉRIMENTAUX

L'appareillage a été décrit dans une publication antérieure[1].

Nous avons utilisé pour cette mise au point les radioisotopes suivants: ^{45}Ca, $^{89 \text{ et } 90}$Sr, ^{140}Ba, ^{228}Ra et ^{226}Ra.

1. *Baryum ,,marqué''*

Quelques mg de $BaCl_2.2H_2O$ pour analyse ont été ,,marqués'' par ^{140}Ba obtenu soit à Harwell, soit à partir d'un échantillon d'uranium irradié un mois à la pile; à cet effet, à une solution nitrique de cet uranium irradié (0.1 g U), ajouter 75 mg de $Sr(NO_3)_2$ dissous dans un peu d'eau et faire trois précipitations successives par HNO_3 fumant; ^{140}Ba ,,carrier free'' est entraîné quantitativement. Remettre le précipité en solution et ajouter 14 mg de $BaCl_2.2H_2O$; précipiter une première fois par HCl 12*N*, redissoudre et reprécipiter par le mélange HCl 12*N* – éther (4/1 : v/v), dissoudre à nouveau, ajouter quelques mg de $FeCl_3$ et précipiter ce dernier par NH_4OH; centrifuger et transférer le liquide surnageant dans un nouveau tube; précipiter $BaCO_3$ par addition de Na_2CO_3. Centrifuger et laver le précipité avant de le redissoudre par HCl dilué; terminer par 3 précipitations par HCl 12*N* pour s'assurer d'une pureté radiochimique suffisante (activité sensiblement constante des précipités successifs).

2. *Radium*

Nous avons utilisé essentiellement deux sources.

(a) Le mésothorium I (^{228}Ra; $T = 6.7$ ans; $E_{(\beta)} = 0.05$ meV) extrait de nitrate de thorium par coprécipitation avec $BaCl_2$; à 1-3 g de $Th(NO_3)_4$, ajouter 10-20 mg de $BaCl_2$; dissoudre dans le minimum d'eau, puis précipiter le mélange des chlorures ($BaCl_2 + RaCl_2$) par addition de plusieurs volumes de HCl 12*N*; répéter 3 fois le processus de précipitation.

Rappelons que ^{228}Ra a pour descendant direct ^{228}Ac (émetteur β; $T = 6.13$ h; $E_{(\beta)} = 1.55$ meV). De plus, durant les 2 à 3 semaines qui suivent la séparation, ^{228}Ra est accompagné du ^{224}Ra (ThX; $T = 3.64$ j; émetteur α) et de ses produits de filiation qui ont tous une vie courte; parmi ceux-ci, le compteur β n'enregistre pratiquement que les rayonnements de ^{212}Pb (ThB; $T = 10.6$ h) et ^{212}Bi (ThC; $T = 60.5$ min) dont l'activité décroît évidemment avec la période du ^{224}Ra. Après une vingtaine de jours, l'activité β se stabilise au 1/3 environ de l'activité initialement mesurée après l'équilibre ^{228}Ra-^{228}Ac, (avec les compteurs GM courants, on détecte seulement le rayonnement de ^{228}Ac).

(b) Le ^{226}Ra émetteur α ($T = 1590$ ans). Une ancienne source contenant principalement ^{226}Ra et un peu de MsTh1 (^{228}Ra), a été purifiée par trois coprécipitations successives, avec quelques mg de $BaCl_2$, par le mélange HCl 12*N* – éther (4/1 : v/v).

C'est le mélange des chlorures alcalino-terreux additionné du $BaCl_2$,,marqué'' par ^{140}Ba (extrait comme ci-dessus) qui, dissous dans quelques ml du mélange éluant, a servi aux essais de reproductibilité de la séparation Ba – Ra (prises de 1 ml par essai; environ 1 mg $BaCl_2$).

Les compteurs β courants n'enregistrent pratiquement que l'activité due aux deux principaux émetteurs β dérivés du radon; RaB (^{214}Pb; $T = 27$ min) et RaC (^{214}Bi; $T = 20$ min); on observe donc une croissance de l'activité avant la période du radon (3.8 j).

ESSAIS DE SÉPARATIONS

A. *Séparation Ba–Ra*

Nous avons d'emblée obtenu des séparations Ba – Ra très convenables avec l'éluant déjà utilisé: méthanol – HCl 12*N* (100/5: v/v).

La Fig. 1 montre le résultat de l'une des quatre élutions Ba(+^{140}Ba) – ^{226}Ra, faites successivement sur la même colonne en vue d'éprouver la reproductibilité de la méthode. Les quatre essais ont fourni des résultats identiques. Les mesures indiquées pour Ba sont celles relevées 15 jours après l'élution, pour Ra, 5 mois plus tard.

Dans chaque essai, la quantité de $BaCl_2$ inactif, marqué par ^{140}Ba introduite est de 1 mg environ et celle de ^{226}Ra peut être estimée à moins de $10^{-3}\gamma$; on peut, dans ce cas, être assuré que l'élément est bien ,,carrier free'' du fait de l'absence d'isotope stable pour Ra.

Sur la Fig. 2, nous avons représenté à une plus grande échelle, la partie de la courbe située entre les deux pics. On peut juger de l'efficacité de la séparation en considérant

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que à ce moment, l'activité de ^{140}Ba au sommet de pic atteignait 4000 c/min, tandis que celle de la portion No. 19 précédant celle où l'on enregistre les premières traces de radium, n'était plus que de 10 c/min au maximum, soit moins de 2.5/1000 de l'activité au sommet. Il va de soi qu'une colonne plus longue améliorerait encore la séparation déjà très bonne.

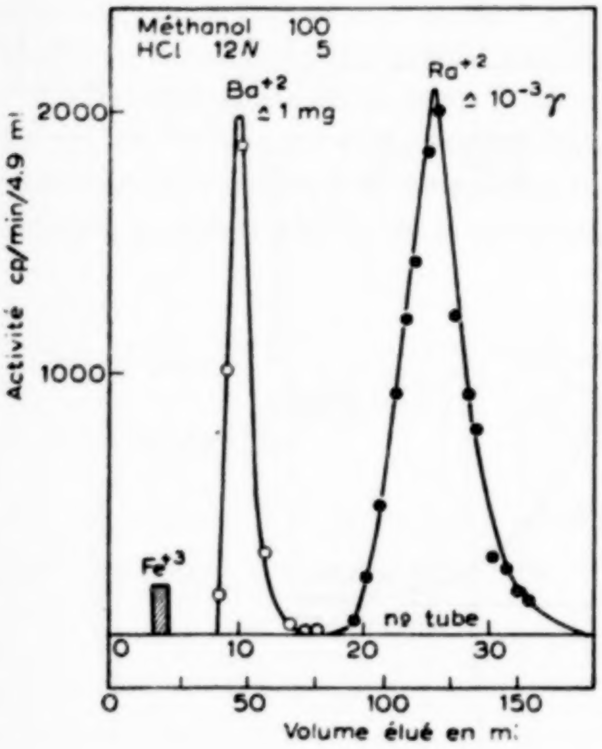

Fig. 1.

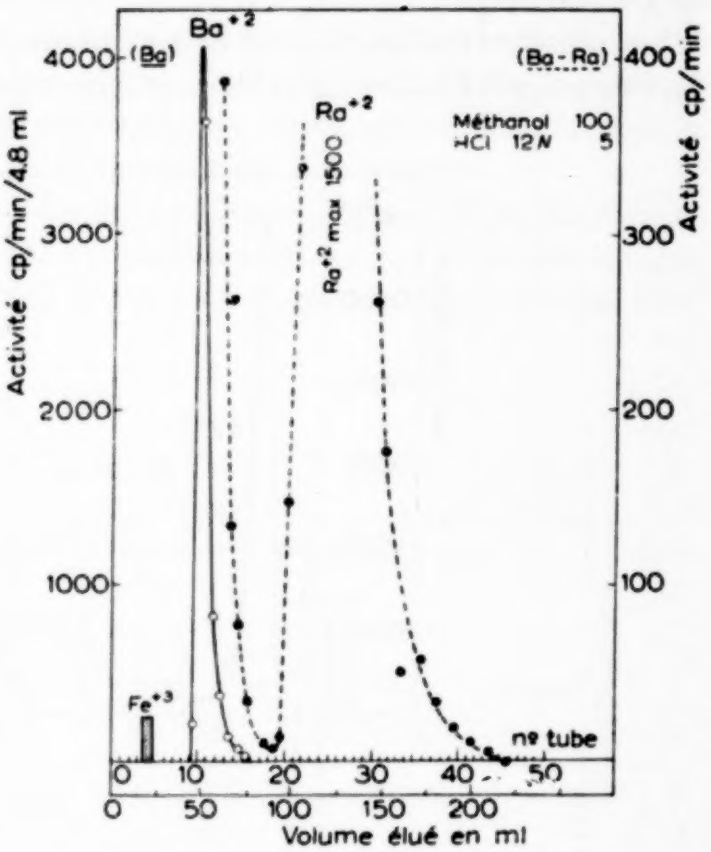

Fig. 2.

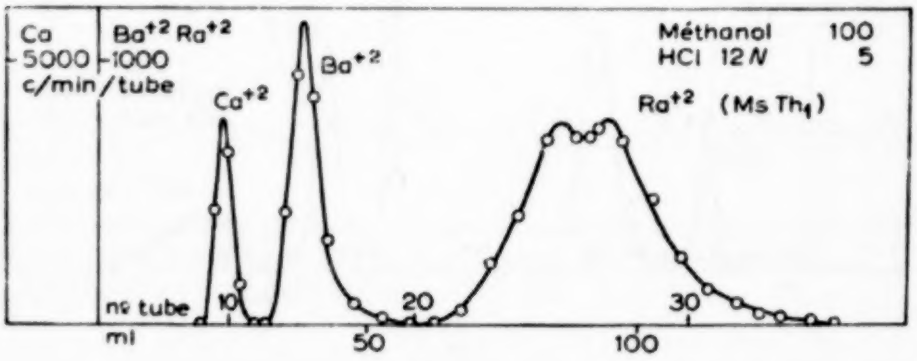

Fig. 3.

La présence éventuelle de Ca n'enlève rien à la qualité de cette séparation comme le montre la Fig. 3 obtenue avec ^{45}Ca-^{140}Ba (1 mg)-^{228}Ra (MsTh 1).

La méthode nous paraît donc particulièrement convenir pour la préparation de sources de mésothorium exemptes de baryum entraîneur; elle pourrait peut-être également être utile au dernier stade de la purification du radium, après les séparations Ba-Ra par cristallisations fractionnées[6,7] ou mieux, après une concentration assez rapide du radium par quelques coprécipitations fractionnées des chromates Ba-Ra, en milieu homogène selon un procédé récemment proposé[8].

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B. Séparation Ca-Sr

Le mélange éluant méthanol-éther-HCl (75-25-5: v/v) utilisé précédemment pour la séparation Ba-Sr, convient également pour la séparation Ca-Sr en doses traceurs; la Fig. 4 se rapporte à une élution de ^{45}Ca accidentellement contaminé par un peu de ^{90}Sr (celui-ci a été identifié par la décroissance de ^{90}Y et la recroissance correspondante du pic de ^{90}Sr).

Les mesures indiquées sont celles obtenues après l'équilibre radioactif ^{90}Sr-^{90}Y; ce dernier migrant entre Ca et Sr perturbe initialement la mesure de la séparation.

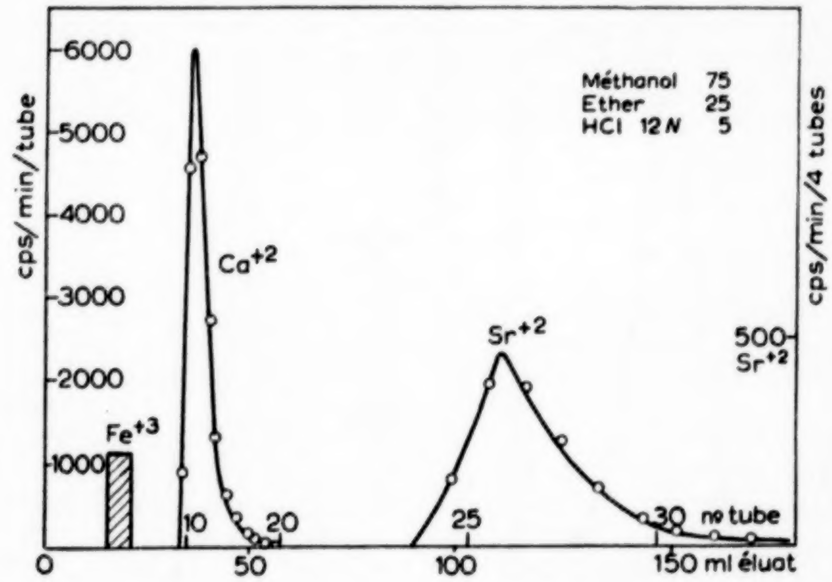

Fig. 4.

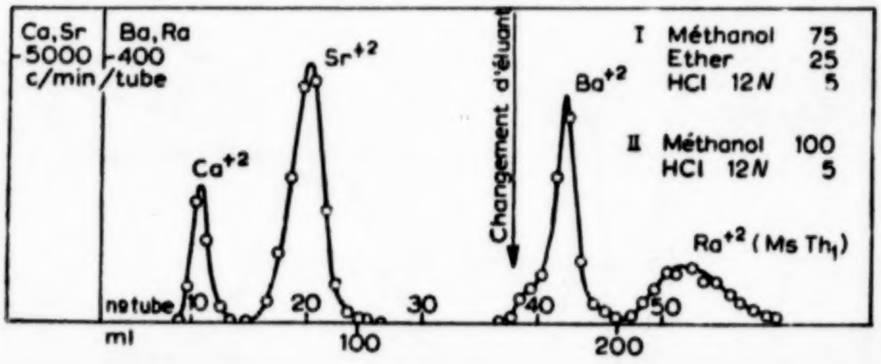

Fig. 5.

C. Séparation des alcalino-terreux Ca-Sr-Ba-Ra en doses traceurs

En utilisant les deux éluants renseignés ci-dessus (éluant à l'éther d'abord), on obtient une séparation très convenable des alcalino-terreux suivants: Ca-Sr-Ba-Ra en quantités impondérables, comme le montre la Fig. 5, (^{228}Ra est carrier free; Sr $\leq 0.001\gamma$; Ba $< 0.8\gamma$; Ca sans support visible).

Le ^{228}Ra (MsTh1) nécessaire à cette séparation avait au préalable été séparé du baryum entraîneur au cours d'une élution préliminaire faite sur une plus petite colonne de 9 cm de long et 2 cm de diamètre, et pour ne pas introduire de quantité appréciable de baryum, seules les dernières fractions de $^{228+224}$Ra ont été utilisées.

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D. Séparation ^{89}Sr-^{140}Ba *(carrier free)*

Nous croyons également intéressant de signaler une séparation ^{89}Sr-^{140}Ba faite sur colonne de cellulose en utilisant les deux éluants préconisés; les isotopes ont été obtenus à l'état „carrier free" à partir d'un échantillon de nitrate d'uranyle irradié environ deux semaines à la pile de Mol. ^{89}Sr et ^{140}Ba sont coprécipités quantitativement avec $Pb(NO_3)_2$ par addition de HNO_3 fumant (3 fois)[9]; le dernier précipité est dissous dans 1 ml de méthanol additionné du minimum d'eau nécessaire et la plus grande partie du plomb est précipitée à l'état de $PbCl_2$ par addition de HCl 12*N*; $PbCl_2$ centrifugé n'entraîne que fort peu Sr et Ba[10]. Cette dernière solution est conservée dans un flacon traité au diméthyldichlorosilane et utilisée directement sur la colonne.

La Fig. 6 indique les mesures faites après l'équilibre radioactif ^{140}Ba-^{140}La. La mesure du pic de ^{140}Ba a pu se faire directement sur les fractions d'élution non évaporées, par comptage γ au compteur à scintillation (Well type). Le rectange hachuré marqué Fe^{+3} indique le volume libre de la colonne.

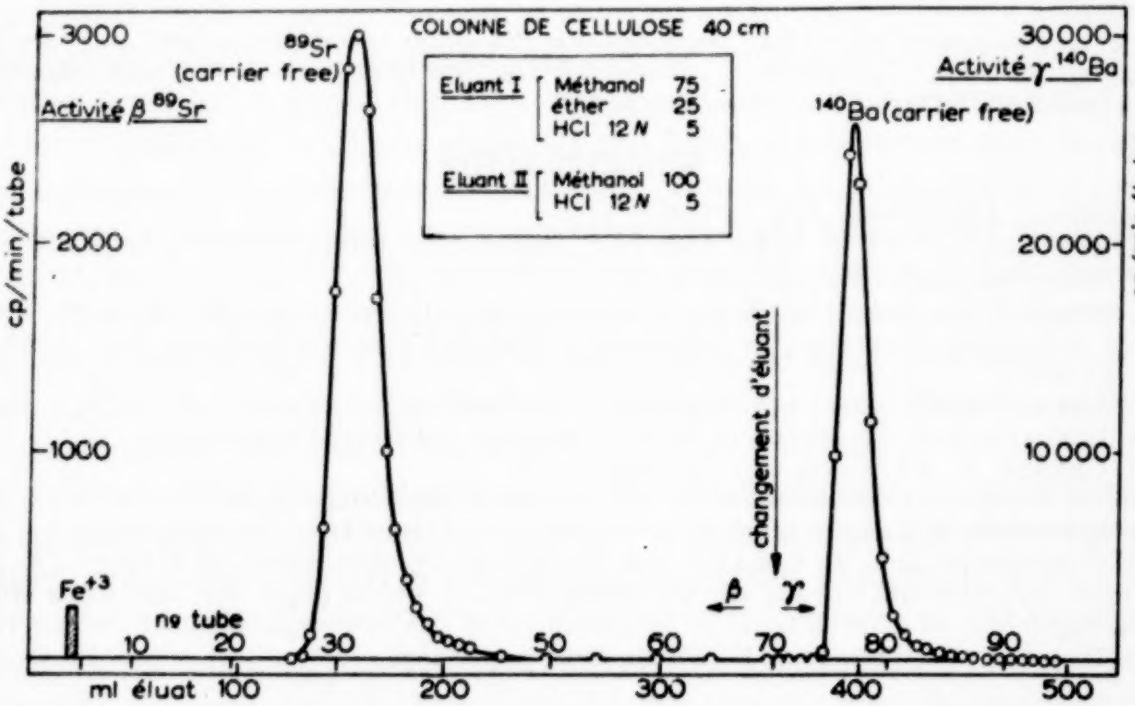

Fig. 6. Séparation chromatographique sur colonne de cellulose d'un mélange ^{89}Sr-^{140}Ba de fission „carrier free". ^{89}Sr est séparé au moyen de l'éluant I, ensuite, ^{140}Ba avec l'éluant II. La composition des éluants étant donnée v/v sur le graphique.

CONCLUSIONS

1. Le mélange éluant méthanol-HCl 12*N* (100-5; v/v) convient très bien à la séparation Ba-Ra *sur colonne de cellulose* et tout particulièrement à la préparation de sources de MsTh1 (^{228}Ra) et de ^{226}Ra, exemptes de Ba entraîneur.

2. Le mélange éluant méthanol-éther-HCl 12*N* (75-25-5), utilisé antérieurement pour la séparation Ba-Sr („carrier free") sépare de même très bien Ca et Sr.

3. Par l'emploi successif de ces deux éluants, il est possible de séparer convenablement, en une opération, des quantités impondérables des 4 alcalino-terreux Ca-Sr-Ba-Ra.

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RÉSUMÉ

Par chromatographie sur une colonne de poudre de cellulose, on peut obtenir une bonne séparation de quantités impondérables de Ca – Sr – Ba – Ra en utilisant successivement les deux éluants suivants :

1. Méthanol – éther – HCl 12*N* (v/v: 75-25-5) (Ca, Sr)

2. Méthanol – HCl 12*N* (v/v: 100-5) (Ba, Ra)

***L'éluant* 1, que nous avons proposé antérieurement pour la séparation de quantités impondérables de baryum et de strontium, convient très bien pour séparer Ca – Sr (carrier-free) et nous l'avons encore une fois éprouvé avec succès pour la séparation $^{89}\mathrm{Sr}$ – $^{140}\mathrm{Ba}$, obtenue à l'état ,,carrier free'' à partir d'un échantillon de nitrate d'urane irradié à la pile.**

***L'éluant* 2 sépare convenablement Ba – Ra (Ba carrier-free ou non) et peut servir à la préparation rapide de sources de mésothorium I ($^{228}\mathrm{Ra}$) exempte de baryum, ou à la purification de petites quantités de radium.**

SUMMARY

A good separation of tracer amounts of Ca – Sr – Ba – Ra could be obtained by chromatography on a cellulose powder column on using successively the following two eluants:

1. Methanol – ether – HCl 12*N* (v/v: 75-25-5) (Ca, Sr).
2. Methanol – HCl 12*N* (v/v:100-5) (Ba, Ra).

Eluant 1, which has already been proposed for the separation of Ba and Sr in tracer amounts, is well suited for the separation of Ca – Sr (carrier free). A further test of this eluant for the separation of $^{89}\mathrm{Sr}$ – $^{140}\mathrm{Ba}$, obtained carrier-free, from an irradiated uranium nitrate sample, proved to be successful.

Eluant 2, gives a satisfactory Ba – Ra separation (Ba either carries free or not) and may be used for a rapid preparation of mesothorium 1-sources ($^{228}\mathrm{Ra}$), free from barium; it is also recommended for the purification of small quantities of radium.

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THE DETERMINATION OF MICROGRAM AND SUB-MICROGRAM AMOUNTS OF BORON

PART I. ABSORPTIOMETRIC DETERMINATION USING CURCUMIN

by

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INTRODUCTION

Because of the high cross-sectional area of boron for thermal neutrons, this element must be largely absent in all materials used in the construction of atomic piles and permissible upper limits are of the order of one part per million or less. Strict purity control for this element in all raw materials and finished products is thus imperative and has necessitated the development of a large number of routine chemical methods for the determination of microgram quantities of boron in a wide variety of substances. The general principles underlying the methods used for the past ten years by the United Kingdom Atomic Energy Authority may now be published and will be described in this and the following paper. The methods have withstood many years of practical application and in the opinion of the authors constitute the most sensitive and precise chemical techniques available. They should prove helpful in fields other than atomic energy, such as biochemistry and agricultural chemistry, where an accurate determination of traces of boron is required. In all cases the element is separated by distillation as methyl borate and collected in a small alkaline residue in a platinum dish. In the present paper, the absorptiometric determination of the element in distillates will be described. In the following paper, general distillation techniques are outlined and the conditions for concentrating the boron in a distillate to give a residue suitable for absorptiometric assay are described.

There are three main chemical methods at present used for the determination of microgram amounts of boric acid. One technique involves the reaction in nearly concentrated sulphuric acid of boric acid and various anthraquinone derivatives of which the substance 1-1′ dianthrimide gives the most sensitive reaction[1]. A shift in absorption spectra between reagent and boron complex occurs but the shift is not very great and these methods, although generally rapid and convenient, are far from being the most sensitive. A fluorimetric method using benzoin has been described[2] which is capable of greater sensitivity, and finally procedures have been given in which boric acid reacts with acidified solutions of curcumin. The use of curcumin can lead to the most sensitive techniques yet reported but this reagent never seems to have attained much popularity, probably because of the difficulties encountered in its use and the poor precision often reported.

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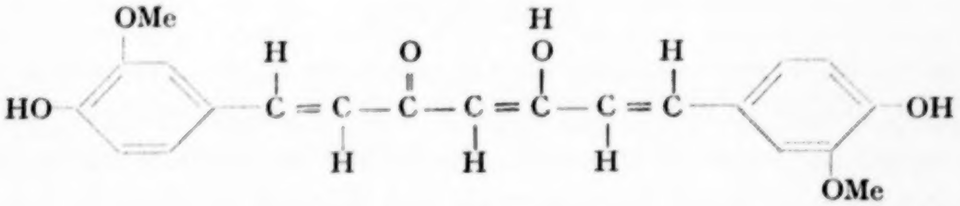
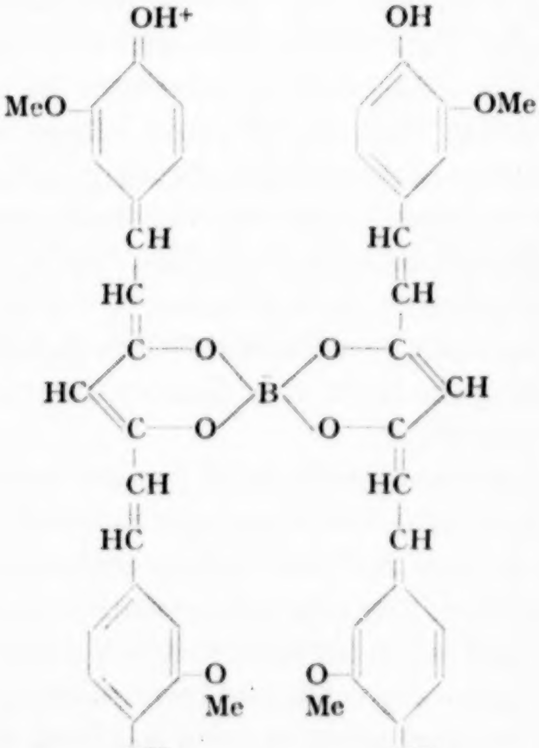
The presence of oxalic acid greatly promotes the formation of a red substance with curcumin, as was first noted by CASSAL AND GERRANS[3], and the technique based on this reaction by NAFTEL[4] is now well known. PHILIPSON has more recently described a procedure using trichloroacetic acid instead of oxalic acid[5].

The red compounds formed between boric acid and curcumin were first isolated and named rosocyanin and rubrocurcumin by CLARKE AND JACKSON[6] who, however, failed to establish their formulae or to realize that they contained chemically bound boron. The present authors[7] have now determined the structure of these compounds and studied their absorption spectra. It was pointed out by KORENMAN[8] that practically all reagents for boron contained an enolic β-diketone group, or amino derivative thereof somewhere in their structure and curcumin is no exception, its formula now being established[9,10,11]



Rosocyanin is a complex monovalent cation containing two curcumin molecules coordinated to a boron atom. The formula for the main "stationary state" of the resulting resonant hybrid is considered[7] to be:



There is almost complete degeneracy in the absorption of the two curcumin chains combined in this complex, each having an oscillator strength near to unity, and the resulting molar absorbancy index of about 180,000 per combined gram-atom of boron, is, according to modern theory, near to the maximum possible light absorption at the wavelength concerned (555 mμ) and within 25-50% of the maximum possible molar absorbancy index for the visible region of the spectrum. The *quantitative* conversion of boron to rosocyanin, therefore, can result in what is effectively the most sensitive absorptiometric method for the determination of this element that can be devised and, in view of the low equivalent weight of boron in the compound, about the most sensitive absorptiometric method that is possible for any element except beryllium.

The use of oxalic acid, which greatly speeds the reaction of boric acid in alcoholic solutions of curcumin, gives rise to another compound, rubrocurcumin, which has nearly the same molar absorbancy index as rosocyanin, per molecule of combined curcumin, but contains only one curcumin molecule per atom of boron instead of two[7]. The formation of rubrocurcumin (which is the main product in methods such as NAFTEL'S) is thus potentially capable of only half the sensitivity of a procedure leading to the production of rosocyanin.

In the first two methods described in this paper alcoholic solutions of curcumin and oxalic acid are used in procedures which originated from the NAFTEL method but which have been greatly modified to give higher precision and sensitivity. Details of the development of these methods will not be given as the research lasted intermittently over many years and a description of it would unduly lengthen the paper. We are satisfied, however, that the procedures described use about the optimum conditions for routine analysis where some precision and sensitivity must be sacrificed for the sake of speed and convenience. In the third method, a radically different approach is used to ensure the complete conversion of all boron to rosocyanin and thus give the maximum sensitivity. This sensitivity is so great (an absorbancy of about 1 for 0.2 μg of boron) that it can prove an embarrassment unless elaborate precautions are used to reduce contamination.

METHODS

Procedure 1

This procedure is applicable to dry ignited residues consisting essentially of 0.02 g of sodium hydroxide-carbonate and containing between 2 and 15 μg of boron as borate.

*Reagents**

Glycerol-sodium hydroxide reagent: Dissolve 1 g of sodium hydroxide, 0.1 g of sodium chloride and 3 ± 0.3 ml of glycerol in 100 ml of water.

Curcumin-oxalic acid reagent: Prepare a litre of a standard alcohol-water mixture by adding water to alcohol (about 35 ml of water is required for 1 l of absolute alcohol) until the specific gravity, corrected for temperature by adding 0.0008 per °C above 15°C, is 0.809 ± 0.0005.

To about 700 ml of this alcohol-water mixture, freshly prepared, add 15.0 g of oxalic acid dihydrate, 12.5 ml of concentrated hydrochloric acid, sp.gr. 1.18, and 85.0 ml of water. When all the oxalic acid has dissolved, add 1.00 g of finely ground pure curcumin (m.p. 182°C) and when this has dissolved, cool the reagent to 20°C and make the volume to exactly 1 l. If a trace of insoluble material remains from the curcumin, this may be neglected, provided that it is allowed to settle out or is centrifuged, and only a clear solution used. The reagent is best stored in soft glass and is stable for many weeks if not exposed to strong sunlight.

Method

The boron will have been separated from the sample by distillation into a 7.5-9 cm platinum dish containing 2 ml of the above glycerol-sodium hydroxide reagent (see Part II).

Evaporate the distillate to dryness on a water bath maintained at a temperature between 85°C and 90°C. Heat the dish to about 150-250°C on a hot plate to remove most of the glycerol. This

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* All reagents should be of analytical quality and tested for freedom from boron.
Notes on the purification of the reagents used in these absorptiometric methods and at other stages in the determination of boron will be found in the next paper.

operation should be performed slowly over a period of at least 10 min and preferably longer. Finally remove the last traces of glycerol by holding the dish over a bunsen flame and then raise the temperature to a dull red-heat for about half a min.

Cool and add 10.0 ml of the curcumin reagent from a pipette, rinsing the sides of the dish with the reagent as it enters. Float the dish upon the surface of a special water bath, kept specifically for the purpose of colour development, the details of which are given below. From time to time during the first 5 min of heating, gently swirl the liquid in the dish and make sure that all the residue has gone into solution. Afterwards leave the dish undisturbed until the contents are dry and allow the dish to remain on the bath for at least a further 3 min to ensure complete dryness and removal of all hydrochloric acid vapour.

Remove the dish from the bath, allow it to cool and add about 10 ml of ethyl alcohol containing not more than 25 or less than 5% by volume of water. Allow the rubrocurcumin to dissolve from the residue, rubbing with a stirring rod provided with a rubber sleeve to assist complete solution. Transfer the extract to a 50 ml graduated flask and rinse the dish thoroughly with small portions of the alcohol–water solution until all coloured matter is removed. Finally make the volume to exactly 50 ml and mix.

Filter the solution through a small, dry, loose textured paper into a 1 cm or 2 cm cell and measure the absorbancy of the solution with a spectrophotometer using light of wave-length 555 mμ, or with a more simple type of absorptiometer using filters having a maximum transmittancy at about this wavelength. Correct the observed absorbancy by that of a blank determination carried out on all reagents exactly as described for the sample. Absorbancies should be measured within 1-2 hours of extracting the rubrocurcumin from the dishes, or fading is appreciable. The dry residues in the dishes, after colour development are stable for many hours.

Calibration

A linear concentration-absorbancy curve is obtained when using a spectrophotometer, or an absorptiometer with the correct filters, and a factor can be used to relate μg boron to absorbancy. A standard boron solution is most conveniently prepared from analytical quality boric acid. A stock solution of 1.43 g of H_3BO_3 in 250 ml should be diluted 1-100 for use. 1.00 ml of the resulting solution contains 10 μg of boron.

Add a standard quantity of boron as boric acid to a 7.5-9 cm diameter platinum dish containing 2 ml of glycerol–sodium hydroxide reagent. Duplicate determinations at the 10 μg level are generally sufficient to establish a calibration factor.

Treat as described above. A little carbon may remain in the dish after ignition but this causes no interference.

Calculate the factor F where

$$F = \frac{\text{sum of } \mu\text{g B added}}{\text{sum of net absorbancies}}$$

F should be of the order of 10 for 1 cm cells, corresponding to about 55% conversion to rubrocurcumin of the boron initially in the platinum dish.

Colour development bath

Control of the water bath used for the evaporation of residues with the curcumin–oxalic acid reagent is the most important step in the curcumin method when a high precision is required. The formation of rubrocurcumin only occurs, in quantity, during the evaporation of the last few ml of a solution and is critically dependent upon the amount of water left in the dish at this stage. This necessitates not only a strict reproducibility of water content in the initial reagent, but a high reproducibility of atmospheric moisture conditions during the evaporation. The rate of evaporation also requires close control to ensure that the boric acid lost after esterification to ethyl borate (which is a significant fraction of the total boron) is always a constant percentage of the whole.

Dishes should float freely on the surface of a water bath thermostatically controlled between 55°C and 60°C with the stirring adjusted or shielded so that only a slight movement of the water surface or dishes takes place. The dishes should be prevented from striking each other (by wire partitions just under the water surface) and it is best to restrict the number on each bath to about 4-6 with a total water surface area of 500-600 sq. cm. The surface should be protected from direct sun-light or radiant heat. A sheet of plastic held about 1 foot above the bath is useful for this purpose and, at the same time, gives additional stability to the air conditions and acts as a protection against contamination. Finally the temperature of the air surrounding the bath should be maintained at a constant value to ensure that the humidity level of the air directly above the dishes remains constant, largely because of "buffering" by the water surface of the bath. These conditions are best attained by placing the water bath on a large hot plate in an enclosed space, such as a fume cupboard, so that a column of warm air surrounds the bath without any direct radiation falling upon the water surface. The air temperature above the bath, as measured by a thermometer clamped vertically with its bulb 5 cm above the water surface, must exceed 35°C. This measurement is purely empirical but acts as a practical guide to suitable and stable air conditions. If the temperature is much below 30°C, low and erratic extinction values are liable to occur; there is no point in having this air temperature exceed 40-45°C. The above conditions are not difficult to obtain in laboratories where the air temperature fluctuations during the day do not exceed a few °C and the relative humidity of the air does not vary by more than 1-2%. Typical results obtained by this procedure are shown in Table I.

TABLE I

FACTOR 8.85

B added *μg*	*Net absorbancy* *1 cm cell*	*B found* *μg*	*Error* *μg B*
1.0	0.100	0.88	−0.12
2.0	0.225	1.99	−0.01
3.0	0.330	2.92	−0.08
4.0	0.440	3.89	−0.11
5.0	0.570	5.04	+0.04
7.5	0.855	7.57	+0.07
10.0	1.14	10.1	+0.1
12.5	1.41	12.5	—
15.0	1.71	15.1	+0.1
20.0	2.27*	20.1	+0.1
25.0	2.83*	25.0	—
27.5	3.13*	27.7	+0.2

* Solution diluted appropriately before measurement.
Standard deviation 0.10 μg B
Reagent blank equivalent to 0.3 μg B.

The importance of local atmospheric control during colour development does not appear to have been fully realised previously but it is the major factor in the attainment of the highest precision by the curcumin method. When the precision need only be of the order of 10%, most of the above elaborations are unnecessary and a simple water bath held at a temperature of about 60°C is all that is required. Such an arrangement can also be used for more precise work if a standard is evaporated with each batch of samples but the factor so obtained will not necessarily remain constant from day to day and the general precision of results is still not as satisfactory as is possible with the more exact control of humidity conditions.

Procedure 2

This procedure is applicable to dry ignited residues consisting essentially of 0.02 g of sodium hydroxide-carbonate and between 0.5 and 4 μg of boron as borate.

Curcumin–oxalic acid reagent

The standard alcohol–water mixture is prepared as described in procedure 1 above and used in the same way to prepare the curcumin reagent except that the quantities of the additives are changed to 15.0 g of oxalic acid dihydrate, 25.0 ml of concentrated hydrochloric acid, sp.gr. 1.18, 75.0 ml of water and 0.35 of finely ground pure curcumin. The reagent is best stored in soft glass and should not be kept for longer than one or two weeks.

Method and calibration

This is essentially the same as in procedure 1, except only 5.0 ml of the curcumin–oxalic acid reagent are used and the absorbancy is measured in a 4 cm cell. The concentration-absorbancy relationship is again linear and duplicate determinations at a 3 μg level should be sufficient to establish the calibration factor:

$$F = \frac{\text{sum of } \mu\text{g B added}}{\text{sum of net absorbancies}}$$

which will be of the order of 3.

The production of rubrocurcumin per unit weight of boron in the platinum dish is rather less efficient by this method than with procedure 1, but the absorbancies of blank determinations, which arise largely from coloured decomposition products of curcumin, are smaller and more reproducible. This procedure is thus more precise when less than about 4-5 μg of the element is to be determined and typical results are shown in Table II.

TABLE II

FACTOR 2.95

B added μg	*Net absorbancy* *1 cm cell*	*B found* μg	*Error* μg *B*
1.00	0.330	0.97	−0.03
1.00	0.310	0.91	−0.09
2.00	0.670	1.98	−0.02
2.00	0.670	1.98	−0.02
3.00	1.00	2.95	−0.05
3.00	1.02	3.01	+0.01
3.00	1.02	3.01	+0.01
4.00	1.37	4.04	+0.04
4.00	1.40	4.13	+0.13
4.00	1.36	4.01	+0.01

Standard deviation 0.06 μg B.
Reagent blank equivalent to 0.1 μg B.

Procedure 3

This procedure should only be used when the highest possible sensitivity is necessary and is applicable to dry ignited residues consisting essentially of 0.004 g sodium hydroxide–carbonate and between 0.01 and 0.2 μg of boron as borate.

Instead of about 50% conversion of boron to rubrocurcumin, as in the previous methods, the boron is almost quantitatively converted to rosocyanin, resulting in a method of four times the intrinsic sensitivity. The small but variable blank absorbancy found by this technique, even in the complete absence of boron, arises from a red decomposition product of curcumin and this blank cannot be eliminated. The disadvantage is largely overcome by taking measurements at two wavelengths with each determination and making use of the different spectral characteristics of the curcumin decomposition and of rosocyanin proper.

Reagents

Glycerol–sodium hydroxide reagent: Dissolve 0.4 g of sodium hydroxide and 1.0 ml of glycerol in 100 ml of water.

Curcumin solution : Dissolve 0.125 g of finely powdered pure curcumin in 15 ml of pure acetone and dilute to 25 ml with water. This solution should be stored in soft glass for not longer than one week.

Acetic acid : 5% by volume in water.

o-chlorophenol reagent : The *o*-chlorophenol used direct in this method and also in the following mixture should be redistilled (176°C) before use, after first washing with 50% sulphuric acid and drying over sodium sulphate. To 12 ml of purified *o*-chlorophenol, add 2.0 ml of 60% perchloric acid and then, whilst stirring, 3.0 ml of acetic anhydride. Store in a dark bottle and reject if reagent becomes coloured.

Method

The boron will have been separated from the sample by distillation into a 5 cm platinum dish (about 2 cm in height) containing 1 ml of the above glycerol–sodium hydroxide reagent (see Part II).

Evaporate the distillate and remove the glycerol by heating on a hot plate as described in Procedure 1. Warm gently over a bunsen flame to remove the last traces of glycerol, then heat to bright redness to fuse the residue. Cease heating immediately all carbon disappears.

Cool and add 1.0 ml of water, washing down any solids from the side of the dish, and then add 0.40 ml of curcumin solution from a 1.00 ml graduated pipette. Neutralise by the dropwise addition of 5% acetic acid until the colour of the curcumin changes to yellow. Add 1 drop of acid in excess and evaporate on a boiling water bath until quite dry and then leave a further 5 min.

Pipette 1.00 ml of redistilled *o*-chlorophenol into the dish and cover the dish with a bakelite cover. Heat the dish on an oil bath at 50°C for about 5 min, swirling the contents to extract all solids. Add 0.200 ml of *o*-chlorophenol reagent, swirl the dish to mix the contents and then leave the dish covered and undisturbed on the oil bath at 50°C for exactly 15 min (within 0.5-1 min). Remove the dish and dilute the contents *immediately* with 2-5 ml of ethyl alcohol containing about 15% by volume of water. The contents of the dish may be further extracted at leisure and the combined extracts made to 10.0 ml in a measuring flask to give a solution stable for several hours.

Filter the solution through a small, dry, loose textured paper or remove solids by centrifugation, and measure the absorbancy of the solution in a 4 cm micro-cell with a spectrophotometer at 550 mμ (A_1) and 630 mμ (A_2). Calculate the boron present in the dish from the expression:

$$\mu\text{g B} = F\,(A_1 - 1.95 A_2)$$

where F is an experimentally determined factor of the order of 0.2.
Determine, in a similar manner, the boron present in a blank determination.

Calibration

The factor F should be determined experimentally and checked for each new batch of reagents. Add 1.00 ml of boric acid solution, containing exactly 0.2 μg of boron, to a 5 cm platinum dish containing 1 ml of glycerol–sodium hydroxide reagent. Evaporate and ignite as described in Procedure 1, and develop the rosocyanin as described in Procedure 3. Carry out a blank determination on reagents alone. At least two determinations with added boron and two blanks should be made.

Calculate the value (A_1—1.95 A_2) for each determination including those for blanks and subtract the mean value obtained for blanks from those to which boron had been added.

Calculate the factor from

$$F = \frac{\text{sum of } \mu\text{g B added}}{\text{sum of net } (A_1 - 1.95\,A_2)}$$

Results obtained by this procedure are shown in Table III.

INTERFERING SUBSTANCES

As the formation of rubrocurcumin or rosocyanin is carried out after boron has been separated by distillation, the problem of interference should not arise, as the distillation effects the removal of all foreign substances. However, in practice, unless elaborate precautions are taken, a milligram or so of the material from which the boron is being

TABLE III

FACTOR $F = 0.18$

B added µg	*Absorbancy* 55 mµ (A_1)	*Absorbancy* 630 mµ (A_2)	*Corrected absorbancy* $(A_1 - 1.95A_2)$	*B Found* µg
Blank	0.267	0.109	0.054	0.010
Blank	0.272	0.115	0.048	0.009
Blank	0.273	0.120	0.039	0.007
0.005	0.315	0.117	0.087	0.007*
0.005	0.316	0.123	0.076	0.005*
0.005	0.300	0.138	0.061	0.002*
0.20	1.345	0.130	1.09	0.187*
0.20	1.38	0.136	1.11	0.191*
0.20	1.39	0.140	1.12	0.193*
0.50	3.08**	0.19	2.71	0.48*
1.00	6.04**	0.24	5.57	0.99*

* Mean blank 0.009 µg deducted.
** Solution diluted appropriately before measurement.
Standard deviation for 24 determinations at 0.005 µg B = 0.0015 µg B.
,, ,, ,, 12 ,, ,, 0.2 µg B = 0.011 µg B.

distilled may spray over into the platinum dish or be carried over as a volatile acid if hydrolysis of salts has occurred in the distillation flask.

The only element known to interfere directly, by forming a substance analogous to rubrocurcumin or rosocyanin, is germanium. As this element has an equivalent weight nearly ten times that of boron, the interference on a weight basis is greatly reduced and, because no methyl ester is formed, interference from the element may generally be disregarded. Other elements present to the extent of a milligram or so give no interference unless they complex with the boron or destroy the curcumin by oxidation. Generally the curcumin will either be completely destroyed or suffer no attack, but the slight effect of manganese, which gives a weak colouration, may arise from the formation of coloured oxidation products of the curcumin by promoting atmospheric attack. Large amounts of organic matter, which may distil by virtue of volatility or the formation of a methyl ester, can cause complications by leaving excessive amounts of carbon when residues are ignited prior to colour development. The presence of salts reduces the amount of coloured complex formed by a given amount of boron. The amount of sodium hydroxide added as the glycerol-sodium hydroxide reagent should not be increased at all in procedure 3 or by more than about 50% when using procedures 1 or 2.

Fluoride interferes at all levels by competing with the curcumin for boron. No practicable method has been found to prevent this interference and fluoride must be completely absent.

The only other substances found, in practice, to cause serious trouble are perchlorates and nitrates, or nitrites, all of which can be carried over into the platinum dish during distillations. The presence of significant quantities of these anions is noted when dried residues are ignited to remove all glycerol before colour development. A fusion of the residue in the platinum dish then occurs. Should this happen, the effects of perchlorate or nitrate can be minimized or eliminated by heating the dish at dull red heat for one minute or longer until all evolution of gas from the melt ceases. The fusion and gas evolution is quite characteristic of perchlorate and should not be confused with the melting which may occur if any alkali residue is very strongly ignited (900-1000°C) for prolonged periods. In all cases when fusion occurs, the residue in the dish should be brought into solution with the minimum quantity (a few drops) of water, which is prevented from creeping up the sides of the platinum dish as much as possible, and the solution is then evaporated gently to dryness on a water bath and dried for a few minutes at about 100°C before treating the residue with the curcumin reagent.

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The work here described, which was carried out in the laboratories of the Chemical Inspectorate, Ministry of Supply, when the authors were members of the staff of that Inspectorate, formed part of a programme extending over many years and resulted from the co-operation of many workers with the authors. It is wished to acknowledge, in particular, the assistance of Miss K. ALLAN, Messrs. E. BOWELL, R. W. CRIPPS, W. FURNESS, A. H. HOLLOWAY, Miss J. STRACHAN AND Mr. A. H. WRIGHT.

SUMMARY

Three methods are described for the absorptiometric determination of boron present in alkaline residues in a platinum dish. These are based on the reaction of boric acid and a curcumin reagent to form the red compounds rubrocurcumin and rosocyanin. The first method is suitable for quantities of the element between about 2 and 15 μg, the second is best used when between 0.5 and 4 μg are present and the third when the highest sensitivity is required, 0.01-0.2 μg. The last method does not involve the use of an oxalic acid promotor and is thought to give the maximum sensitivity possible for any absorptiometric technique. The three procedures were developed and have been used over the last decade for the analysis of atomic energy materials and have received very thorough testing under routine conditions.

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COULOMETRIC TITRATION OF URANIUM AND URANIUM-VANADIUM MIXTURES WITH +3 TITANIUM

by

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LINGANE AND IWAMOTO[1] described a method for the coulometric titration of +6 uranium to the +4 state with titanous ion electrogenerated by reduction of +4 titanium at a mercury cathode. This method is highly accurate and serves well for the precise assay of uranium compounds, but it suffers from awkwardness associated with the use of a mercury cathode and requires an elevated temperature.

In a recent study in this laboratory[2] the conditions under which titanous ion can be electrogenerated with 100% current efficiency at a platinum cathode have been delineated, and it was shown that ferric ion, ceric ion, and +5 and +4 vanadium can be titrated very successfully by use of a platinum generator cathode provided a moderately concentrated (6 to 8 *F*) sulfuric acid solution of titanyl sulfate is used as supporting electrolyte. This same technique has been found to be equally successful for the titration of +6 uranium to the +4 state, and is not only more convenient manipulatively than the LINGANE AND IWAMOTO method but also has the advantage of not requiring a heated solution. Furthermore, the method is applicable to the analysis of uranium-vanadium mixtures.

To define optimum conditions for the titration a systematic study was made of the factors which influence the rate of reduction of +6 uranium by titanous ion. The rate of the reaction was followed by electrogenerating a known amount of +3 titanium in the test solution containing known concentrations of +6 uranium and sulfuric acid. The rate of oxidation of the +3 titanium was observed by the rate of decay of the current between two identical platinum indicator electrodes subjected to a constant applied voltage. At the applied voltage used (400 mV) the uranium species do not contribute to the amperometric indicator current. The current results solely from reduction of +4 titanium (present in relatively large concentration) at the cathode and the oxidation of +3 titanium at the anode. Thus the well poised cathode serves as reference electrode and the anode is the indicator electrode. The instantaneous current is a measure of the extant concentration of +3 titanium.

The variables studied were the concentrations of +4 titanium, +6 uranium, +4 uranium, kind and concentration of acid, and temperature. The experimental rate equation in sulfuric acid solution was found to be

$$\frac{-d(\mathrm{Ti}^{+3})}{dt} = \frac{k(\mathrm{Ti}^{+3})^2\ (\mathrm{U}^{+6})}{(\mathrm{Ti}^{+4})\ (\mathrm{H_2SO_4})} \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

where the parentheses denote formal concentrations, except in the case of (H_2SO_4) which is the conventional thermodynamic activity of the ions of sulfuric acid. The rate is seen to be second order in respect to the concentration of +3 titanium, first order in respect to both the concentration of +4 titanium and the activity of the sulfuric acid. The rate is independent of the concentration of +4 uranium. At 30°C the specific rate constant k has the value $5.2 \cdot 10^8$ min^{-1}, and its temperature coefficient is approximately 9%/deg.

It will be noted that the reaction rate decreases with increasing sulfuric acid concentration. However, as discussed in a previous paper[2], a moderately large (6-8 F) concentration of sulfuric acid is necessary to obtain 100% current efficiency in the generation of +3 titanium by reduction of +4 titanium at a platinum cathode.

We conclude that the reduction of +6 uranium by +3 titanium proceeds stepwise, first to the +5 and then to the +4 states. The rate determining step is the reduction of +5 uranium. A likely mechanism is

$$U^{+6} + Ti^{+3} = U^{+5} + Ti^{+4} \quad \text{(fast)}$$

$$U^{+5} + Ti^{+3} = U^{+4} + Ti^{+4} \quad \text{(slow)}$$

The rate determining reduction of +5 uranium is too slow for a practical titration at room temperature. At an elevated temperature (*e.g.*, 80°) at which the reaction is fast enough for a satisfactory titration, the electrogeneration of +3 titanium at a platinum cathode becomes less than 100% current efficient[2]. We have found that the reaction can be effectively catalyzed at room temperature by a small amount of ferrous ion.

In 8 F sulfuric acid the formal potential of the ferric-ferrous couple is more oxidizing than the potentials of the U^{+6}-U^{+5} and U^{+6}-U^{+4} couples, but it is several tenths of a volt more reducing than the potential of the U^{+5}-U^{+4} couple. Therefore, ferrous ion must act as a catalyst by reducing +5 uranium to the +4 state more rapidly than does +3 titanium, and the ferric ion formed is reduced relatively rapidly by the +3 titanium.

TITRATION TECHNIQUE

The titration cell consisted of a 200 ml tall form lipless beaker closed by a rubber stopper. The generator cathode was a platinum foil with an area of 14.9 cm^2. The auxiliary anode was a platinum wire in 1 F sulfuric acid, contained in a glass tube, whose bottom was closed by a sintered glass disc, and which was immersed in the test solution. Air was removed from the test solution with nitrogen, and a magnetic stirrer provided efficient stirring. The constant current source has been described by LINGANE[3]. Conditions for 100% current efficiency have been reported previously[2].

The amperometric e.p. detection system comprised two identical platinum electrodes (area 1 cm^2 each) across which 250 mV applied voltage was maintained. The indicator current was observed in terms of the iR drop across a 1000 ohm series resistor, the total applied voltage being appropriately readjusted to compensate for the iR loss and maintain the voltage across the indicator electrodes constant.

Up to the e.p. the indicator current remains at a small value determined by the concentration of ferrous ion used as a catalyst, Beyond the e.p. the indicator current, now governed by the depolarization of the indicator anode by excess +3 titanium, increases linearly. A convenient method of locating the equivalence point is to take a few indicator current readings before and after the e.p., and extrapolate to the intersection of the two linear segments of the curve.

The optimum supporting electrolyte is 6 to 8 F sulfuric acid containing 0.6 F titanyl sulfate. As discussed in a previous paper[2], with this electrolyte current efficiency for reduction of +4 titanium remains at 100% up to a generating current density of 3 mA/cm^2.

Known amounts of +6 uranium were obtained in the form of a solution of uranyl acetate, which had been standardized by reduction to the +4 state with zinc and titration with dichromate[4].

PERFORMANCE DATA

Table I presents the results of 113 titrations of 8 to 225 mg quantities of +6 uranium in a volume of *ca.* 100 ml. In all cases, 10 mg of ferrous ammonium sulfate (to yield a concentration of 0.25 mM ferrous ion) was added to the air-free supporting electrolyte as a catalyst. To correct for a small amount of ferric ion impurity in the ferrous ammonium sulfate, the supporting electrolyte was first pretitrated to the e.p. before the uranium sample was added.

It is evident that there is no significant systematic error in the titration, and its precision appears to be limited only by the care exercised in the measurements. The titration should prove useful for the precision assay of uranium compounds.

TABLE I

COULOMETRIC TITRATION OF URANIUM

The supporting electrolyte (volume *ca.* 100 ml) consisted of 8 F sulfuric acid, 0.6 F titanic sulfate, and 0.2 to 0.3 mM ferrous ion as a catalyst. Generating current densities from 1.3 to 3 mA/cm^2 were used. Air was removed from the solution with nitrogen.

Uranium *taken* mg	*Uranium* *found (average)* mg	*No. of trials*	*Error (average)* %
224.7	224.6	3	−0.05
179.7	179.7	8	0.00
134.8	134.7	13	−0.07
89.86	89.83	18	−0.03
46.07	46.06	4	−0.02
44.93	44.95	19	0.04
35.70	35.70	7	0.00
26.78	26.77	11	−0.04
17.85	17.86	17	0.06
8.925	8.923	13	−0.02

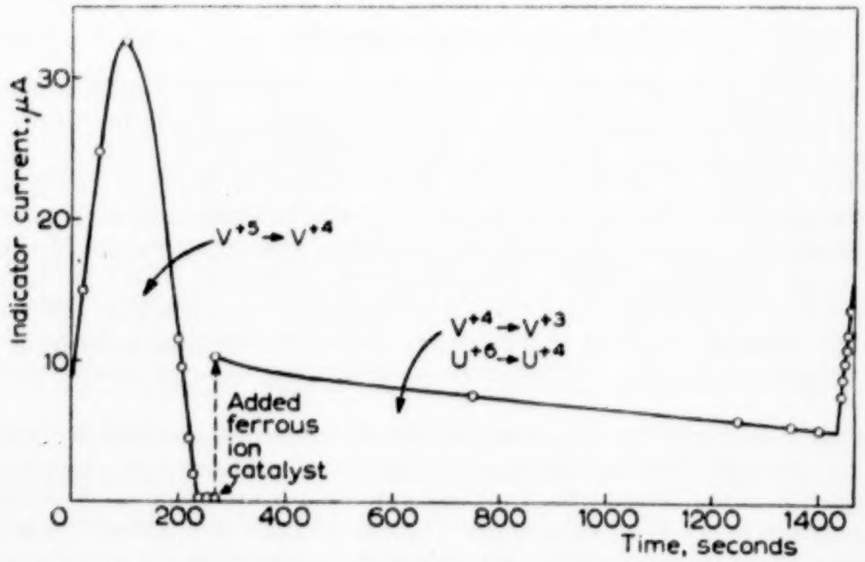

Fig. 1. Amperometric titration curve of 4.65 mg of +5 vanadium and 44.93 mg of +6 uranium in 100 ml of supporting electrolyte (0.6 F titanyl sulfate in 8 F sulfuric acid). The applied voltage across the platinum indicator electrodes during the first stage (up to 250 seconds) was 350 mV. After the addition of 10 mg of ferrous ammonium sulfate as catalyst, the applied voltage was decreased to 250 mV for the remainder of the titration.

From the characteristics of the titration of vanadium alone[2] and uranium alone, it was expected that this titration should be applicable to vanadium–uranium mixtures using amperometric e.p. detection. This has been realized, and typical performance data are shown in Table II.

TABLE II

TITRATION OF URANIUM–VANADIUM MIXTURES

The supporting electrolyte (volume *ca.* 100 ml) consisted of 8 *F* sulfuric acid and 0.6 *F* titanic sulfate. 10 mg ferrous ammonium sulfate catalyst was added after the first end-point (see Fig. 1).

Uranium *taken*	*Uranium* *found*	*Error*	*Vanadium* *taken*	*Vanadium* *found*	*Error*
mg		*%*	*mg*		*%*
92.14	92.11	0.0	5.096	5.082	−0.3
92.14	92.12	0.0	4.463	4.460	−0.1
44.93	44.89	−0.1	4.647	4.651	+0.1
44.93	44.78	−0.3	4.647	4.644	−0.1
44.93	44.84	−0.2	4.518	4.542	+0.5
44.93	44.94	0.0	4.463	4.451	−0.2
44.93	44.91	0.0	2.171	2.160	−0.5
44.93	45.06	+0.3	2.171	2.165	−0.3
44.93	44.86	−0.2	0.736	0.730	−0.8
42.77	42.73	−0.1	0.736	0.732	−0.5
17.85	17.81	−0.2	18.56	18.53	−0.2
17.85	17.86	+0.1	17.96	17.98	+0.1
17.85	17.84	−0.1	9.558	9.540	−0.2
17.85	17.83	−0.1	9.294	9.295	0.0
17.85	17.84	−0.1	8.981	8.993	+0.1

Fig. 1 shows the amperometric titration curve of a mixture of 4.65 mg of +5 vanadium and 44.93 mg of +6 uranium in 100 ml of supporting electrolyte (0.6 *F* titanyl sulfate in 8 *F* sulfuric acid). The first stage of the titration (e.p. at 230 sec) corresponds to the titration of +5 vanadium to the +4 state. During the second stage (230 to 1440 sec) the +4 vanadium is reduced to the +3 state simultaneously with the reduction of +6 uranium to the +4 state.

Shortly after the first e.p. was passed ferrous ion (10 mg of ferrous ammonium sulfate) was added as a catalyst, and the indicator current is governed by the reduction of ferric ion and +4 titanium at the indicator cathode. During this second stage the solution contains a small concentration of ferric ion from the equilibria

$$Fe^{++} + V^{+4} = Fe^{++} + V^{+3};\, K = 0.23$$

$$2Fe^{++} + U^{+6} = 2Fe^{+++} + U^{+4};\, K = 0.01$$

The equilibrium constants pertain to 8 *F* sulfuric acid and were evaluated from the observed formal potentials of the several couples. The decrease in the indicator current up to the second e.p. reflects the decreasing equilibrium concentration of ferric ion.

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The time between the two end-points corresponds to the sum of $V^{+4} \rightarrow V^{+3}$ and $U^{+6} \rightarrow U^{+4}$, and the uranium content is obtained by subtracting twice the time to the first e.p. from the total time to the second e.p.

The ferrous ion catalyst must not be added until after the +5 vanadium has been titrated to the +4 state. Ferrous ion is quantitatively oxidized by +5 vanadium. A mixture of +5 vanadium and ferric iron shows an amperometric titration curve with two maxima and two minima. The first minimum corresponds to the e.p. for the titration of V^{+5} to V^{+4} and the second occurs after the simultaneous reduction of V^{+4} to V^{+3} and Fe^{+++} to Fe^{++}. (The statement about this titration in the 11th line on p. 472 of our previous paper[2] is erroneous.) Both end-points are well defined and a mixture of +5 vanadium and ferric ion can be analyzed accurately. However, if +6 uranium is also present there is no distinct indication of the e.p. for the reduction of Fe^{+++} to Fe^{++} before reduction of +6 uranium begins. Consequently it is not possible to employ this titration for the analysis of a mixture of vanadium, iron, and uranium.

Table II summarizes results obtained in titrating mixtures of +5 vanadium and +6 uranium, with uranium predominating.

Vanadium can be titrated accurately in the presence of a 50-fold excess of uranium, a situation commonly encountered in practice, as well as when only a small amount of uranium is present. The determination of uranium is accurate provided that it predominates, or at least is present in not much smaller amount than the vanadium. Because the uranium determination depends on the prior titration of the +5 vanadium (see Fig. 1) its accuracy deteriorates when vanadium predominates.

SUMMARY

Coulometric titration of +6 uranium with electrogenerated titanous ion at a platinum cathode in 8 *F* sulfuric acid can be performed accurately in the presence of ferrous ion as a catalyst. Amperometric end-point detection is employed. The titration is suitable for the precise assay of uranium compounds. Mixtures of +5 vanadium and +6 uranium can be titrated, because the reduction of +5 vanadium occurs at a more oxidizing potential than the reduction of +4 vanadium and +6 uranium. Using amperometric end-point detection, two end-points are observed corresponding to the reduction of +5 vanadium to the +4 state, and to the simultaneous reduction of +4 vanadium to the +3 state and +6 uranium to the +4 state. Errors are as small as ± 0.3%, provided the uraninium/vanadium ratio is between 0.1 and 10.

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ELECTROLYTICALLY GENERATED SILVER(II) AS A COULOMETRIC TITRANT

by

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This study was initiated to determine the feasibility of using electrolytically generated silver(II) as a coulometric titrant. NOYES and his coworkers[1] studied thoroughly the properties of silver(II) solutions. In a previous paper[2] we demonstrated the use of AgO as an oxidimetric reagent for the determination of manganese, cerium, and chromium.

MEIER AND SWIFT[3] attempted to employ electrogenerated silver(II) in coulometric titrations, but were dissuaded by the competing reduction of silver(II) by water, and delay in the response of the amperometric indicator current. Systematic investigation of the factors which govern the current efficiency of oxidation of argentous ion at platinum and gold anodes in various media has revealed that the use of a gold anode, ice-cold solutions, and a fairly high concentration (4 to 6M) of nitric acid, provides 100% current efficiency. Furthermore, at a temperature below 5° the rate of reduction of silver(II) by water is so greatly suppressed that it no longer interferes. We have also found that pre-oxidation of the platinum indicator electrodes eliminates the delay in either amperometric or potentiometric response.

CURRENT EFFICIENCY FOR THE ELECTROGENERATION OF SILVER(II)

Current efficiencies for the oxidation of argentous ion in various acid media were estimated from current-potential curves with and without argentous ion present. The cell was a 100 ml weighing bottle closed by a rubber stopper. The generator anode was of gold or platinum foil with an area of 2 cm². The cathode was a platinum wire spiral separated from the test solution in a glass tube, whose bottom was closed with a sintered glass disk. The catholyte in this tube was 1 M sulfuric acid and its level was maintained above that of the solution in the cell. The cell was cooled by surrounding it with crushed ice. A magnetic stirrer provided efficient stirring.

The potential of the anode was measured against an external saturated calomel electrode which was placed in contact with the solution in the cell by means of a salt bridge containing a solution of the acid under test.

Typical current-anode potential curves are shown in Fig. 1. The effect of argentous ion concentration is illustrated. These curves were measured in 5M nitric acid. It was found early in the study that only nitric acid was a usable generation media. In all other acids tried either 100% current efficiency was not attained, or silver(II) was so unstable that oxidation of water became seriously competitive with the oxidation of the sample.

The current efficiency for the generation of argentic ion as a function of current density, temperature, and kind of anode, is shown in Fig. 2. These curves were derived from the current potential curves by assuming that the current efficiency is given by the following equation:

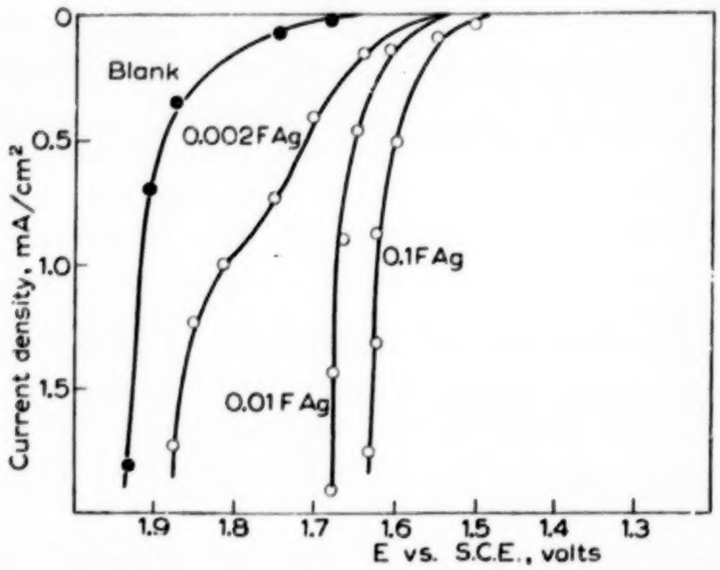

Fig. 1. Current–potential curves for the oxidation of silver(I) to silver(II) in $5M$ HNO_3 at 0°C.

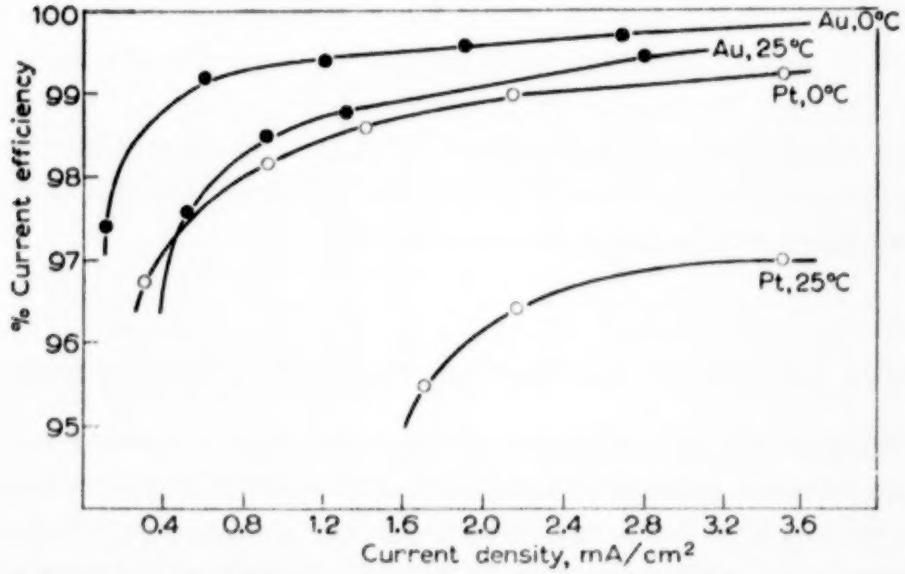

Fig. 2. Effect of current density, temperature, and anode material on the current efficiency in $5M$ HNO_3 containing $0.1M$ argentous nitrate.

$$\% \text{ current efficiency} = \frac{i - i_0}{i} \times 100$$

where i is the total current at a given anode potential and i_0 is the current observed at the same potential with the acid solution alone.

It is evident from Fig. 2 that current efficiencies closer to 100% are attained with a gold generator anode than with platinum, because gold has a higher oxygen overpotential. A gold anode was used for all titrations. A high current density is desirable and the size of the generator anode should be chosen such that a current density greater than about 2.0 milliamp/cm^2 is obtained. Increasing current density increases the current efficiency because the slope of the current-potential curve for the oxidation of argentous ion is greater than the slope of the curve for the oxidation of water. This divergence of the current-potential curves continues only up to the limiting current density for the oxidation of argentous ion. When the limiting current density is approached, the two current-potential curves begin to merge, and the current efficiency decays. (See the curve for 0.002 *F* argentous ion in Fig. 1.) One-tenth *M* silver nitrate solutions were used so that the limiting current density (*ca.* 30 milliamp/cm^2) would be well above the current densities normally desirable for the oxidation of the titrate in a convenient time.

A decrease in temperature to about 0°C not only increases current efficiency but also enhances the stability of silver(II) in solution. The current efficiency is increased mainly because low temperatures cause the slope of the current-potential curve for the oxidation of water to decrease, whereas that for the oxidation of argentous ion is slightly increased. When titrations were attempted at room temperature positive errors resulted, both because the current efficiency becomes less than 100% and because the reduction of silver(II) by water competes with its reduction by the sample.

Current efficiencies derived from the current-potential curves may be considerably better than actual titration efficiencies, because oxidation of water by silver(II) competes with that of the substance titrated. For this reason titration efficiencies were determined directly under conditions for which current efficiencies were already known. Only in cold 3 to 7*M* nitric acid was the oxidation of water suppressed sufficiently so that it no longer competed with the oxidation of the sample. In sulfuric, phosphoric, and perchloric acids, titration efficiencies were less than 90%. Argentic ion is stabilized in nitric acid by the formation of the dark brown argentic nitrate complex.

COULOMETRIC TITRATION OF VANADIUM, CERIUM, ARSENIC AND OXALIC ACID

Oxalic acid, cerium(III), arsenic(III), and vanadium(IV) were titrated in a generation medium composed of 5*M* nitric acid and 0.1*M* argentous nitrate. The titration cell was the same as the one used in the study of current efficiencies.

The end-point was detected either potentiometrically or amperometrically. When the potentiometric method was used, the potential of a platinum indicator electrode was measured with reference to a saturated calomel electrode (via a potassium nitrate salt bridge) in the usual manner. The detection of the end-point proved to be difficult due to the familiar slow attainment of stable potentials when the solution potential exceeded about one volt *vs.* S.C.E. ROSS AND SHAIN[4] have attributed this drifting of potential to the oxidation of the surface of the platinum electrode to form a film of platinous oxide. The reality of this film has been demonstrated by ANSON AND LINGANE[5]. Apparently a stable potential is not attained until the oxide film is fully formed.

In titrations with silver(II) potentiometric end-point detection was unsuccessful unless the electrode was pre-oxidized by placing it in a solution of silver(II). Some test substances (oxalic acid and arsenic(III)) rapidly reduced the oxide film and thus could not be determined using potentiometric end-point detection. In the case of cerium, the use of a previously oxidized electrode was not necessary because the oxide film was formed and maintained by the cerium(IV) present once the titration was begun.

Amperometry with two identical platinum electrodes is more generally applicable than potentiometry. As with potentiometry difficulties were observed due to electrode oxidation. In agreement with MEIER AND SWIFT[3], a delay period was observed during which little or no amperometric indicator current was recorded even though excess silver(II) had been generated. No reducible impurities were detectable in the generation medium. Fig. 3, obtained in blank titrations, illustrates this phenomenon. As shown by curve 1, when the platinum indicator electrodes are in the ordinary "reduced" condition the indicator current does not increase with the first excess of silver(II) but remains small until a considerable excess has been generated. When the indicator electrodes are previously oxidized by soaking them in a silver(II) solution, followed by thorough washing, the indicator current begins its linear increase immediately (curve 2).

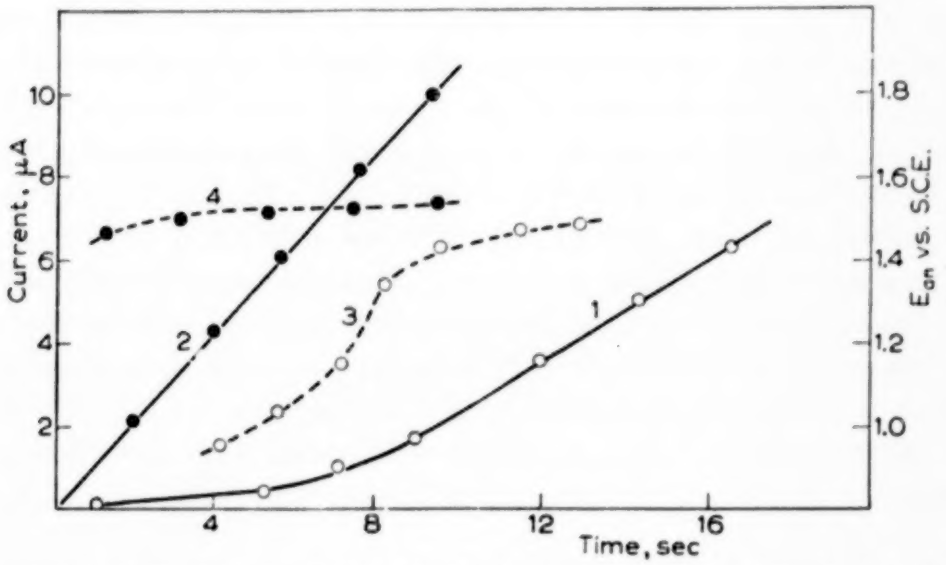

Fig. 3. Amperometric indicator current and indicator potential of oxidized and un-oxidized electrodes. Curve 1: Un-oxidized indicator current. Curve 2: Oxidized indicator current. Curve 3: Un-oxidized anode potential. Curve 4: Oxidized anode potential.

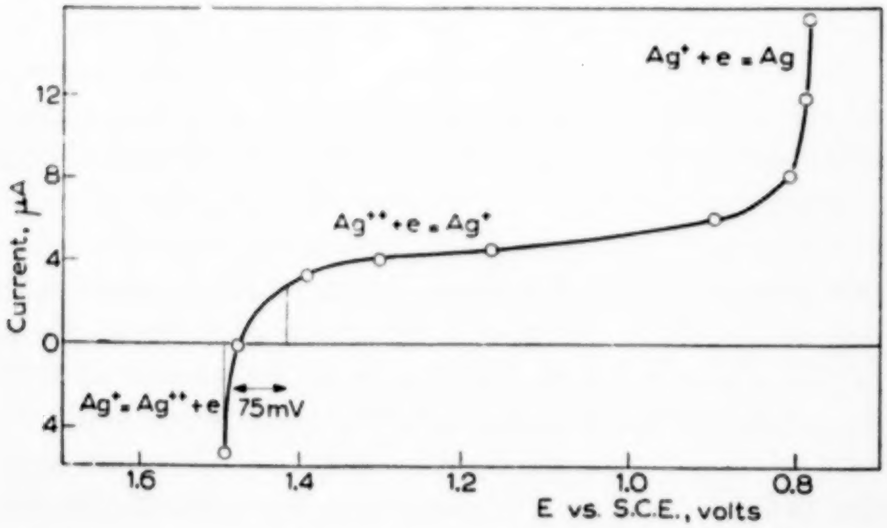

Fig. 4. Current-potential curve of a mixture of silver(I) and (II) in $5M$ HNO_3 at 0°. The concentration of silver(I) was $0.1M$.

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The potential of the indicator anode *vs.* generation time is also shown in Fig. 3 for both oxidized and unoxidized electrodes. When the electrode is pre-oxidized the presence of the oxide film allows oxidizing anode potentials to be attained immediately. When the electrode does not carry an oxide film, anode potentials initially are much below what they would be if the film were present. Apparently no argentous ion can be oxidized at the indicator anode until the anode potential has reached *ca.* +1.2 V *vs.* S.C.E. even though there is argentic ion present to be reduced at the indicator cathode.

Fig. 4 is a current-potential curve of a solution containing both silver(I) and (II). The solid vertical lines, whose position was chosen so that the cathodic and anodic currents would be equal (a necessary condition in two electrode amperometry), indicate the potentials of the indicating electrodes. Since the voltage applied across the indicator electrodes is 75 mV, the lines are set 75 mV apart. It is evident that current can flow only when the anode is more oxidizing than +1.5 V. Little current can flow when the potential of the anode is held below this value while the oxide film is forming. The existence of the delay period is only possible because platinum is oxidized very slowly by the small concentrations of silver(II) present. If the generation is stopped after a few seconds the indicator current will slowly rise from zero, and after about 30 minutes will approach the value characteristic of previously oxidized electrodes.

To avoid the difficulties associated with the oxidation of the electrodes, the indicator electrodes were pre-oxidized in a nitric acid solution of silver(II). To prevent the reduction of the oxide film by the sample the electrodes were not placed in the cell until the end-point had been slightly over-run. (Preliminarily the end-point can be approximately determined with un-oxidized electrodes.) After a slight excess of silver(II) was present, the pre-oxidized indicator electrodes were placed in the solution and generation was continued to determine the slope of the titration line. The latter was then extrapolated back to zero current to define the end-point.

In every case, except cerium, no current was observed before the end-point so no error was incurred by using this procedure. With cerium, the amperometric current was followed throughout the titration since cerium(IV) maintained the oxide film and no difficulties were observed.

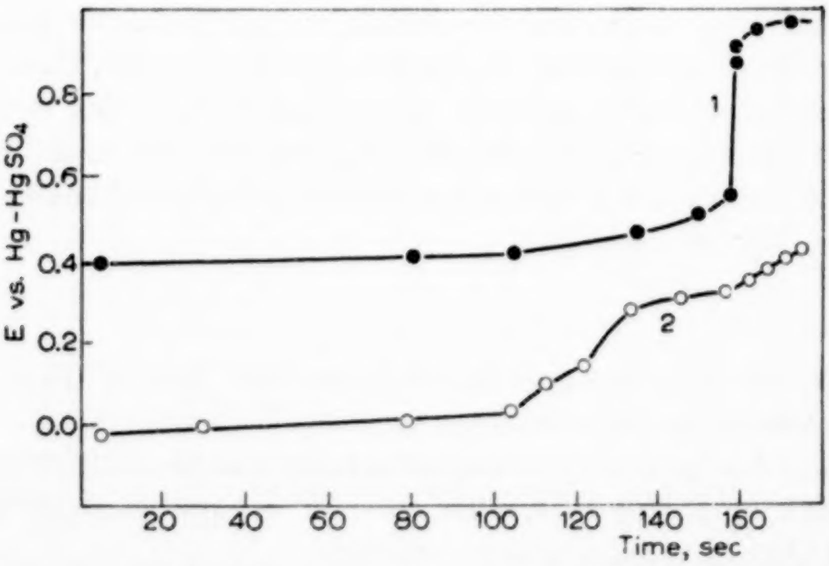

Fig. 5. Titration of vanadium(IV) (10.20 mg) with silver(II) in 100 ml 5 *M* HNO_3 at 0°. 1. Oxidized indicator electrode. 2. Un-oxidized electrode.

Vanadium

Table I shows typical results which demonstrate that vanadium can be determined with an accuracy of ±0.2%. Almost all of the determinations were done potentiometrically. Since vanadium(IV) is not a very strong reducing agent, pre-oxidized electrodes could be left in the solution throughout the titration. Fig 5 shows potentiometric titration curves of vanadium(IV) with oxidized and un-oxidized electrodes. It is evident that the oxidation of the indicator electrode is necessary for both sharp potential inflections and accurate results. Amperometry was also used to determine the vanadium end-point. With an applied potential of 200 mV across the indicator electrodes current was observed only after the end-point when argentic ion became available for reduction at the indicator cathode. The intersection of the current-time curve with the zero current axis was taken as the end-point.

Arsenic and oxalic acid

Table I presents typical data obtained from the titrations of arsenic(III) and oxalic acid.

TABLE I

DETERMINATION OF ARSENIC, VANADIUM, AND OXALIC ACID

Substance	*Taken* *mg*	*No. of trials*	*Found average* *mg*	*Av. error* *%*	*Av. deviation* *%*
Vanadium	20.40	5	20.40	−0.0	±0.1
	10.20	5	10.19	−0.1	±0.1
	2.550	7	2.547	−0.1	±0.1
	1.275	5	1.274	−0.1	±0.1
Arsenic	7.828	10	7.833	+0.1	±0.2
	3.914	7	3.913	0.0	+0.1
	1.957	5	1.958	+0.1	±0.1
	0.9785	5	0.9782	0.0	±0.1
Oxalic acid	9.176	6	9.177	0.0	±0.0
	4.588	5	4.587	0.0	±0.1
	2.294	5	2.294	0.0	±0.1

Both arsenic(III) and oxalic acid are strong enough reducing agents to remove all or part of the oxide film from the electrodes. For this reason these substances were determined amperometrically, and the pre-oxidized electrodes were not introduced into the solution until some excess of silver(II) was present as indicated by the light brown color of the solution. The indicator current, which is virtually nil up to the e.p., increases linearly beyond the e.p.

Cerium

The determination of cerium was found to be more difficult than that of the other substances, because the reaction between cerium(IV) and silver(II) is slow and because the cerous-ceric potential is very nearly as oxidizing as the argentous-argentic potential in strong nitric acid. However, since ceric ion is capable of oxidizing platinum no pre-treatment of the electrodes was necessary.

When cerium was titrated using the orthodox potentiometric end-point technique,

TABLE II

TITRATION OF CERIUM(III)

Taken mg	*Found* mg	*Error* %
12.92	12.99	+0.5%
	12.92	0.0
	12.95	+0.2
	12.97	+0.4
	12.89[a]	—0.2
	12.92[a]	0.0
	12.95[a]	+0.2
	12.92[a]	0.0
	12.91[a]	—0.1
	12.90[a]	—0.2
6.460	6.450	—0.2
	6.470	+0.2
	6.426	—0.5
	6.460[a]	0.0
	6.450[a]	—0.2

[a] Amperometric end-point, all others potentiometric (1.430 V taken as end-point potential).

only a small, ill-defined potential inflection was observed. However, good results were found when the titration was stopped at an arbitrary potential of 1.430 V *vs.* S.C.E. This potential was established by adding an equivalent amount of silver(II) to a standard solution of cerium(III) and measuring the potential. In practice it was necessary, near the end-point, to wait about two minutes after the generation of each increment before steady potentials were obtained. Waiting periods of 15 minutes or more were detrimental because a measurable quantity of silver(II) was reduced by water, causing positive errors. As shown in Table II the titration yields accurate results.

Amperometric end-point detection was also used to advantage. Fig. 6 shows a typical amperometric titration curve taken with two identical platinum electrodes with a potential of 75 mV applied across them. Since the cerous – ceric couple functions quasi-

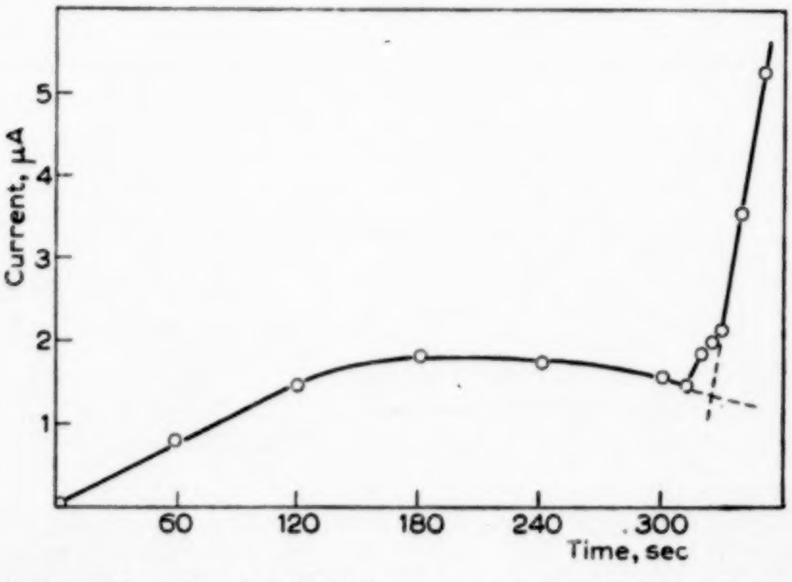

Fig. 6. Amperometric titration of cerium(III) (12.92 mg) in $5M$ HNO_3, $0.1M$ $AgNO_3$ at 0°C. The potential applied across the indicator electrodes was 75 mV.

reversibly a typical maximum is observed about half way through the titration. The current does not fall to zero at the end-point because somewhat before this argentous ion, as well as cerous ion, begins to be oxidized at the indicator anode. Ceric ion before, and both argentic ion after the end-point, are reduced at the cathode. As with the potentiometric titrations, some time had to be allowed near the end-point for equilibrium to be attained. The procedure used was to generate silver(II) until *ca.* 99% of the cerium had been oxidized and then to wait 5 minutes before completing the titration. If less time was allowed, negative errors were found, due to the presence of unreacted silver(II). If more than 15 min was allowed, small positive errors were observed, due to the reduction of some silver(II) by water.

Other attempted determinations

When silver(II) was tried as a coulometric oxidant for manganese and chromium poor results were obtained because the oxidation of these substances was so slow that significant quantities of silver(II) were reduced by water. Manganese and chromium, as well as cerium, can be accurately determined with electrolytically generated silver(II) by generating a large excess of silver(II) and titrating the resultant solution with standard ferrous solution. This method is analogous to the oxidation of the sample by excess AgO as previously described[2].

Reducing agents which are strong enough to reduce nitric acid can be determined if care is taken. For instance, results accurate to ±0.3% were obtained in the determination of ferrous iron. Actually the ferrous iron is oxidized immediately by nitric acid but the oxides of nitrogen produced can be accurately titrated if their escape from solution is prevented. This is accomplished by starting the titration immediately after the introduction of the sample and by stirring as slowly as possible.

ACKNOWLEDGEMENT

Appreciation is expressed to the Mallinckrodt Chemical Works for partial financial support of this study and to the Shell Oil Company for a fellowship held by one of us (D.G.D.).

SUMMARY

The use of electrolytically generated silver(II) as a coulometric titrant has been studied. Difficulties arising from the current efficiency for generation of silver (II) at a platinum or gold electrode and from the reduction of silver(II) by water, have been overcome. The precautions necessary for accurate titrations of oxalic acid, cerium(III), arsenic(III) and vanadium(IV) by amperometric or potentiometric methods are detailed. Manganese and chromium could not be determined directly. Substances which reduce nitric acid could be determined if care was taken.

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DETECTION OF UNCOMBINED OXYGEN IN ZIRCONIUM METAL

by

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INTRODUCTION

Current interest in the use of zirconium as reactor material has led to studies of its oxygen content, since oxygen impurity is known to influence the physical properties, particularly the hardness and ductility of zirconium metal.

Conceivably, oxygen may be present in zirconium in two general states:

1. In the completely combined form as crystalline zirconium oxide.
2. As oxygen on zirconium, held by surface adsorption or possibly by capillary adsorption.

The oxygen-content is dependent upon the nature and treatment of the metal itself. GULDNER AND WOOTEN[1] showed by X-ray diffraction that pure ductile zirconium sheet is capable of adsorbing more than 38 atom per cent of oxygen without the formation of monoclinic zirconium oxide.

DE BOER AND FAST[2] and ALNUTT AND SHEER[3] demonstrated that dissolved oxygen behaves as a negative ion at high temperature and moves toward the anode in an electric field.

Presently known methods of analysis for oxygen do not differentiate between zirconium oxide and other forms of oxygen. Combustion methods[4], in which the oxygen is calculated by difference, can be used only for large percentages of oxygen. In different procedures, zirconium metal may be removed leaving a weighable residue of zirconium oxide. This is accomplished either by the use of chlorine gas[4] or by treatment with dry hydrogen chloride gas[5,6]. The experimental conditions are such that other forms of oxygen may react to form zirconium oxide and be analyzed as such.

This paper describes the analysis of zirconium metal for oxygen which is not present in the combined form of zirconium oxide. When zirconium metal is dissolved in a solution of hydrofluoric acid, a small amount of oxygen may be liberated as molecular oxygen and evolved into the surrounding atmosphere. The oxygen can then be collected and analyzed as free oxygen gas. This is accomplished by absorbing the oxygen into alkaline manganous solution, and then determining it colorimetrically[7] as iodine.

Any oxygen present as zirconium oxide remains as a precipitate or as a zirconyl salt in the hydrofluoric acid solution and, therefore, is not evolved.

PROCEDURE

Apparatus

The equipment used is a modification of that used for the determination of oxygen in helium by the Winkler method, as described by SILVERMAN AND BRADSHAW[7]. The gas sampling bulb is replaced by a solution flask (Fig. 1) for the dissolving of the metallic zirconium.

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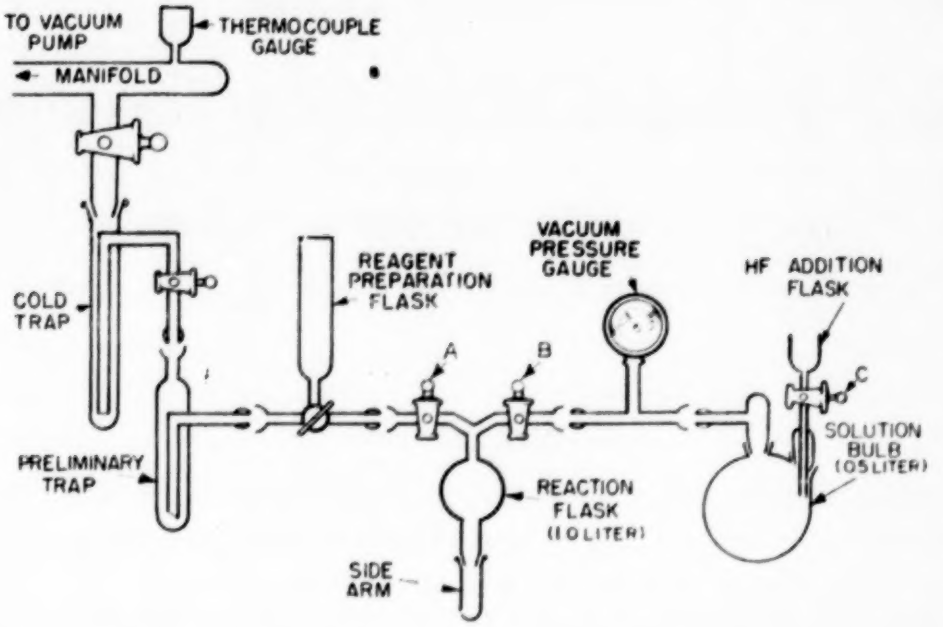

Fig. 1. Schematic apparatus for determination of oxygen in zirconium.

Reagents

Care must be taken in preparing the analytical reagents to prevent the introduction of oxygen or oxidizing materials, which would cause an excessively high blank.

Potassium iodide (0.3N). Prepare fresh daily by dissolving 5 g of potassium iodide in 100 ml of boiling distilled water. Use carbon dioxide purging during the heating and cooling process.

Sodium hydroxide (1.5N). Prepare fresh daily by dissolving 6 g of sodium hydroxide in 100 ml of boiling distilled water. Use helium purging during the heating and cooling process.

Manganous chloride (0.1M). Dissolve 10 g of $MnCl_2 \cdot 4H_2O$ in 500 ml of boiling distilled water which has been slightly acidified with hydrochloric acid. (With carbon dioxide purging).

Hydrofluoric acid (10%). Mix 10 ml of concentrated hydrofluoric acid (48%) and 40 ml of concentrated hydrochloric acid with 50 ml of distilled water. Store in a polyethylene bottle.

o-Xylene ($C_6H_4(CH_3)_2$). Matheson, Coleman and Bell – best grade available.

Analysis

The method is that described for the determination of oxygen in helium[7] with some modifications. Weigh approximately 0.1 g of clean zirconium metal sheet and place it in the bottom of the solution flask, (Fig. 1). Fill stop-cock bore C of the HF addition flask with distilled water to prevent the later addition of oxygen (from the air) through the bore. Assemble the system as is shown in Fig. 1, using a Consolidated grease of suitable temperature range but omit the side arm of the reaction flask. Pipette 10 ml of 1.5N sodium hydroxide solution and 5 ml of 0.3N potassium iodide solution into the side arm. Put the side arm in place and evacuate the entire system, including the solution flask, to less than 5 μ. While the system is being evacuated, pipette 25 ml of the manganous chloride into the reagent preparation flask, pipetting carefully to exclude air bubbles. Put the circular heater in place around the flask. Bring the solution to a boil while purging it with carbon dioxide. Remove the heater and cool the solution with a jet of air directed against the outside of the flask while continuing the carbon dioxide purging.

When the manganous solution is cool and the system has been evacuated, suck the manganous solution into the reaction flask; reserve the last portion of the solution to prevent air leakage.

Check the pressure of the system and when equilibrium has been established close stopcock A. Place 15 ml of the 10% hydrofluoric acid solution in the HF addition flask. Carefully open stopcock C and slowly add the hydrofluoric acid solution to the zirconium without introducing any air. Allow the pressure in the system to come to equilibrium. Read the sample pressure on the vacuum pressure gauge.

Close stopcock B. Disassemble that part of the system up to the reaction flask and place the reaction flask on a mixer (Fig. 2). Agitate the mixture at about 5 r.p.m. for two hours. Re-insert the reaction flask in the vacuum system, in the reverse direction, so that stopcock B is now closest to the vacuum pump. Re-evacuate the system, except the reaction flask, to less than 5 μ.

While evacuating, pipette 20 ml of boiled, purged, distilled water and 5 ml of concentrated hydrochloric acid into the reagent preparation flask. Heat to boiling, with carbon dioxide purging. Cool with continued purging. When the hydrochloric acid solution is cool, suck it into the reaction flask without permitting the entry of air. Add 20 ml of *o*-xylene through the reagent flask to the reaction flask without permitting the entry of air.

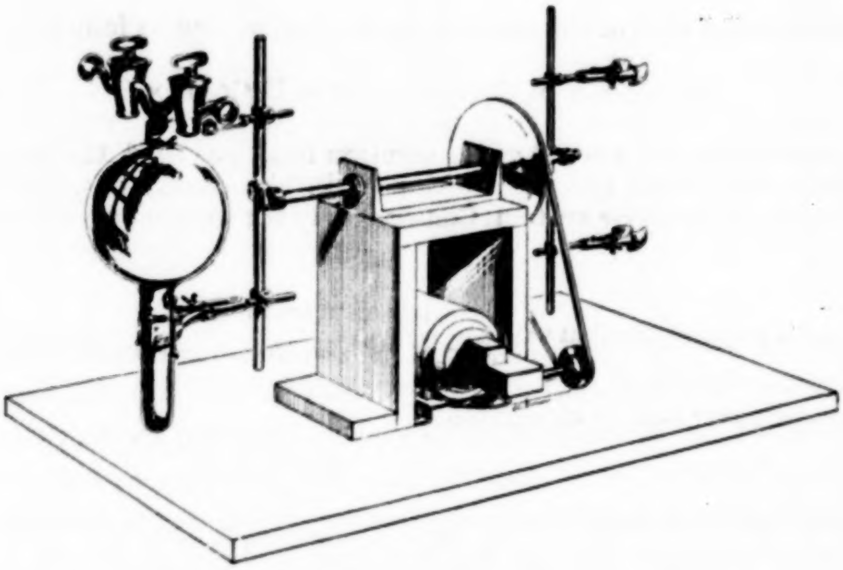

Fig. 2. Mixer (determination of oxygen in zirconium).

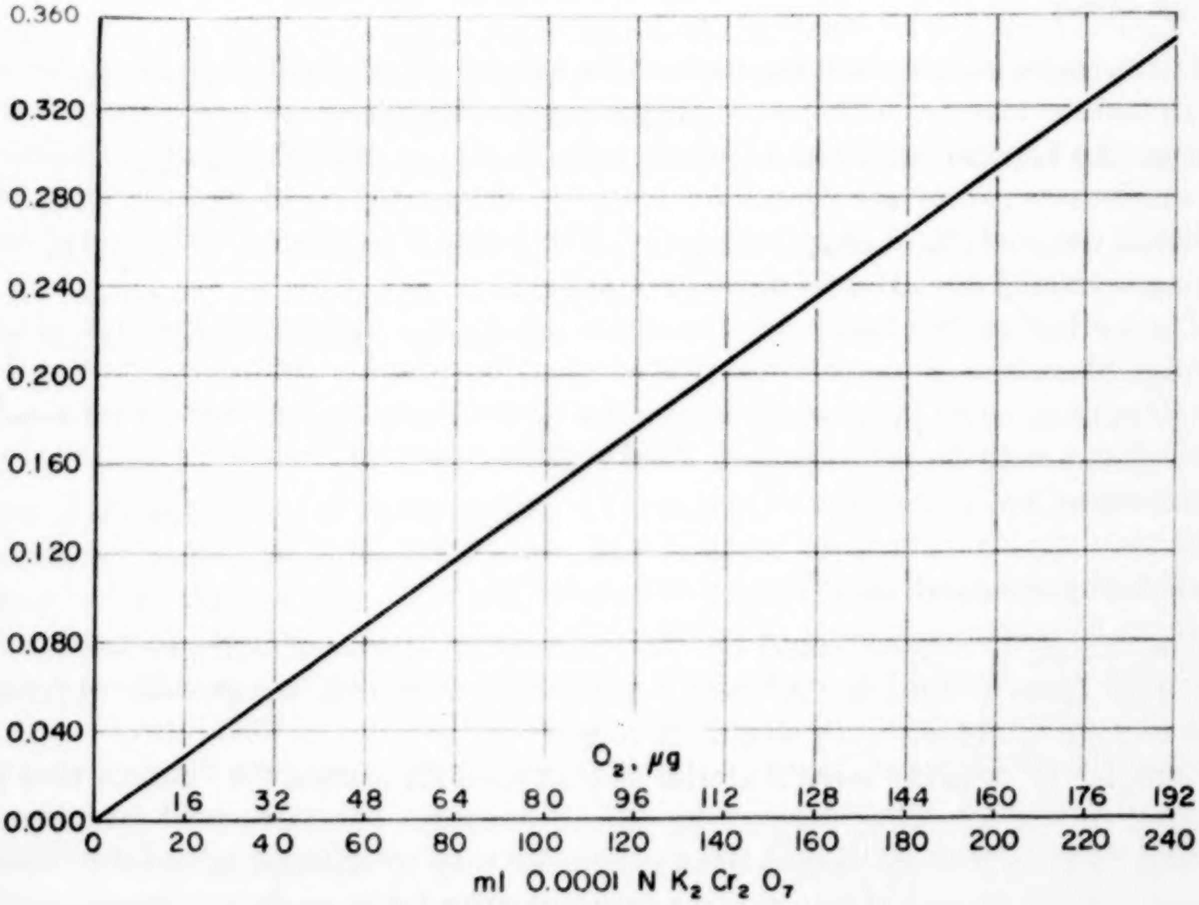

Fig. 3. Absorption of iodine in 10 ml *o*-xylene.

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Close the stopcocks, remove the reaction flask and extract the iodine into the *o*-xylene with gentle shaking to prevent the formation of an emulsion. When the extraction is complete the aqueous layer will be water-white. Open the flask to the atmosphere, drain out the liquid, and separate the two layers. Filter the organic layer through paper into a 25-ml volumetric flask. Dilute to volume with *o*-xylene. Store the solution in the dark until ready to read spectrophotometrically. Read the sample at 495 mμ within the next four hours, using a Beckman, Model DU, spectrophotometer.

Convert the absorbance reading to ml of 0.0001N $K_2Cr_2O_7$ using a standard curve, Fig. 3. Such a curve is prepared by using known amounts of potassium dichromate, in the manner described above[7].

Calculations

The weight of oxygen isolated in the reaction flask is calculated as follows:

$$\text{mg } O_2 = N \text{ of } K_2Cr_2O_7 \times \text{ml of } K_2Cr_2O_7 \times 8 \quad \ldots\ldots\ldots\ldots \quad (1)$$

Since no method of pumping the gas out of the solution flask was used, the sample gas is in equilibrium between the reaction flask and the solution flask. The volume of the reaction flask is two-thirds that of the entire equilibrium system. Consequently the weight per cent oxygen is calculated as follows:

$$\text{wt per cent oxygen} = \frac{\text{mg oxygen found}}{0.667 \times \text{mg zirconium sample}} \times 100 \quad \ldots\ldots\ldots \quad (2)$$

If desired the atom per cent can be calculated:

$$\text{Atom per cent oxygen} = \frac{\dfrac{\text{mg } O_2}{16}}{\dfrac{\text{mg } O_2}{16} + \dfrac{\text{mg sample} - \text{mg } O_2}{91}} \times 100 \quad \ldots\ldots\ldots \quad (3)$$

EXPERIMENTAL RESULTS

Blank values

The changes, which adapt the method for oxygen determination (in gases) to oxygen in zirconium metal, include new reagents and techniques and could consequently change the experimental blank. When a blank, *i.e.*, a reagent sample containing no zirconium was run by the procedure described herein, the blank was the same as that found in the analysis of oxygen in gases[7]. This value is equivalent to 0.004 mg oxygen with a standard deviation of 0.0004 mg oxygen.

The method for this blank determination (absence of zirconium) does not, of course, involve liberation of any hydrogen. The question whether hydrogen, given off from the zirconium, could purge oxygen from the hydrofluoric acid solution, was considered. A blank run with the solution flask filled with hydrogen did not differ from the normal blank value.

Analysis of zirconium samples

The values of oxygen found by this method in various samples of zirconium are listed in Table I. Sample "A" was a sample of zirconium, supposedly oxygen-free. The oxygen found was 0.15 weight % (0.9 atom %).

Sample "B" was the same material as that used for sample "A" except that it was treated in the following manner to absorb oxygen: The sample of zirconium was heated to 1200°F in an oxygen atmosphere for 5 to 10 minutes in order to obtain a pseudo-oxide coating. The oxygen was evacuated and the sample was heated to 1200°F

TABLE I

OXYGEN CONTENT OF VARIOUS ZIRCONIUM SAMPLES
(Other than oxygen as ZrO_2)

Sample	*Zirconium* *mg*	*Oxygen found*				
		mg	*Weight per cent*	*Average weight per cent*	*Atom per cent*	*Average atom per cent*
A	89.6	0.0891	0.10	0.15	0.6	0.9
	45.1	0.0849	0.19		1.1	
B	107.2	0.1097	0.11	0.12	0.6	0.7
	89.5	0.1129	0.13		0.7	
	51.6	0.0665	0.13		0.7	
C	78.0	0.0488	0.06	0.13	0.4	0.8
	79.0	0.1090	0.14		0.8	
	74.2	0.1656	0.22		1.2	

again in order to obtain even distribution of oxygen throughout the sample. The heat-treated sample (sample "B") was analyzed by X-ray diffraction methods and found to contain about 17 atom per cent of total absorbed oxygen. The non-oxide oxygen, as determined by this procedure, was 0.12 weight % (0.7 atom %). Sample "C" was a sample of zirconium sheet of the same quality as that which is used as structural reactor material. The non-oxide oxygen found by this method was 0.13 weight %.

Possibility of peroxide-formation

Known amounts of hydrogen peroxide (equivalent to the weight of oxygen determined by this method) were added to mixtures of zirconium, water, hydrochloric and hydrofluoric acids. The amount of peroxide present could be detected by its particular reaction with chromate-diphenylcarbazide reagent.

The minimum amount of peroxide detectible by the carbazide method is 0.0075 mg (equivalent to 0.0047 mg oxygen).

Test samples of zirconium, water and the two acids alone did not give a positive test for peroxide. Consequently the oxygen found by this method (50 to 170 mg) could not be due to peroxide formation.

DISCUSSION

The exact chemistry of the solution of zirconium metal in aqueous hydrochloric-hydrofluoric acid solution is not known. The possible sources of oxygen that would be detected by the analytical method are in the water and in the metal sample itself.

The possibility that oxygen is liberated from water by any combination of zirconium metal, hydrofluoric acid or hydrochloric acid need not be considered. The possibility that the oxygen found by our method is due to peroxide-formation is eliminated, since synthetic samples containing zirconium, water, the two acids and hydrogen peroxide (equivalent to the oxygen determined) show positive tests for intentionally added peroxide while the zirconium test runs do not. On the other hand, the stability of zirconium oxide which is well known, precludes the possibility of its break-down into zirconium plus oxygen in hydrochloric-hydrofluoric acid medium. The quantities of oxygen found by our method (50 to 170 μg) are well above the blank of this procedure (4 μg).

The deviations in results are not unexpected and can be attributed to "sampling error" since only very small samples of zirconium were taken. It is known that oxygen which has been absorbed into zirconium may not be evenly distributed. However, a deviation of only 0.01 weight % (0.1 atom %) oxygen was obtained with sample "B", which had been heat-treated to obtain even oxygen distribution.

CONCLUSION

Microgram amounts of oxygen evolved when zirconium is dissolved in hydrofluoric acid solution, can be determined quantitatively by the method described in this paper. The range of the method is 1 to 200 μg with a blank of 4 ± 0.4 μg. Reasonable precision, namely a deviation of 0.01 weight % (0.1 atom %) oxygen, can be obtained if the sample is homogeneous in oxygen content.

SUMMARY

This study was undertaken to develop a means of determining oxygen in zirconium which is present in a form other than that of zirconium oxide.

The method described determines oxygen which is evolved as molecular oxygen when solid zirconium metal is dissolved in hydrofluoric acid solution. The oxygen evolved is caught in a separate flask and ultimately determined colorimetrically as iodine. In this procedure, the oxygen held as ZrO_2 is not evolved and is not determined.

The range of oxygen determined by this method was between 50 to 170 μg which is equivalent to 0.06 to 0.22% oxygen. The deviation was ± 0.01% oxygen.

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THE SUCCESSIVE POLAROGRAPHIC DETERMINATION OF As(III) AND As(V)

by

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INTRODUCTION

Up to the present time no method has yet been described for the successive polarographic determination of As(III) and As(V). This is due to the fact that As(V) has been found not to be reducible in polarography. Only one exception has been found, *viz.* the case in which 11.5*M* HCl was the base solution[1]. In this medium a double wave is formed, corresponding to the reduction As(V) — As — AsH_3 and leaving no possibility for a stepwise determination of As(V) and As(III). Moreover, the disadvantage of using this medium is that i_d/c increases with increasing concentration of As(V) above 0.4 m*M*. Hence, for the purpose mentioned in the heading an indirect way was followed.

HEYROVSKÝ[2] suggested that two polarograms should be recorded: one before and one after reduction of As(V) to As(III) by means of a suitable reducing agent, *e.g.* hydrazine in concentrated sulphuric acid. This agent had already been used by KRJUKOWA for the polarographic determination of As in contact-sulphuric acid[3] and phosphoric acid[4].

As far as the authors are aware of this suggestion of HEYROVSKÝ has never been tried out. We thought it worthwhile to investigate its possibilities. It promised to be attractive because sulphuric acid appears to be the best medium for getting a reasonably developed polarographic diffusion current for As(III)[5], whereas the reduction of As(V) by hydrazine does not introduce interfering ions into the solution.

EXPERIMENTAL

Stock solutions of As(III) and As(V) were prepared from As_2O_3 and As_2O_5 by dissolving the reagents in NaOH, followed by neutralizing with H_2SO_4. From these stock solutions different solutions were prepared, all containing 0.01% gelatin as a maximum suppressor and 1*N* H_2SO_4 as a supporting electrolyte.

It has been reported that gelatin is not a suitable maximum suppressor since it causes a reduction of the arsenic wave height[6], but in accordance with experiments of COULSON[7], published after our work had been finished, we have not met with any difficulty in our measurements due to using gelatin.

All polarograms were obtained with the automatic pen-recording Radiometer Polarograph type PO 3 using the dropping mercury electrode assembly type E 63. Nitrogen was passed through the solution before each run. The drop time was 2 to 3 sec at room temperature.

The arsenic wave consists of two main parts. The first wave with a half-wave potential of —0.66 V *vs.* S.C.E. is directly proportional to the concentration. The second wave is poorly defined, so all data are related to the first wave, half-wave potential and diffusion current being measured as described by WILLARD *et al.*[8].

A typical polarogram of As(III) in $1N$ H_2SO_4 is shown in Fig. 1.

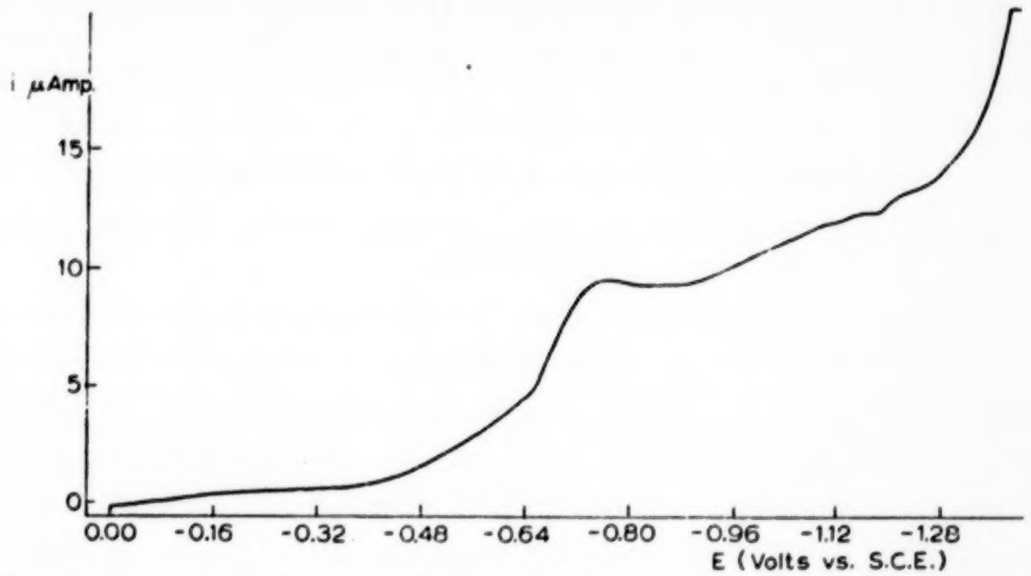

Fig. 1. Polarogram of As(III). Concentration of As(III): $37 \cdot 10^{-5} M$. Supporting electrolyt: H_2SO_4 N. Maximum suppressor: gelatin, 0.01%. Damping: 3. Amplifier sensitivity: 65. Compensation condensor current: 0.

RESULTS

1. Polarograms were recorded of As(III)-solutions with different concentrations. The results listed in Table I show a satisfactory proportionality of i_d with concentration.

2. The influence of hydrazine sulphate and As(V) on the As(III) curves was traced. Hydrazine sulphate (HS) was found to interfere when present in a concentration above 150 mg/100 ml. Above this concentration, the plateau was less pronounced and the wave height decreased. As expected, As(V) had no perceptible influence, not even at a concentration 15 times greater than that of As(III).

3. Preliminary experiments showed that As(V) was reduced by heating with HS in concentrated sulphuric acid. We traced the influence of variations in HS concentration, acid concentration and heating time. The results are listed in Table II. Good results were obtained with about 100 mg HS per 100 ml final solution of at most 10^{-3} M As, sulphuric acid concentrations of at least 45% and a heating time of about ten minutes. After reduction the solutions were made $1N$ to H_2SO_4 and 0.01% to gelatin as already noted before.

4. Finally, we determined the total arsenic content of solutions containing known amounts of As(III) and As(V), after reduction had been performed with HS in concentrated H_2SO_4, by heating for 10 min. Table III shows that the errors are of the same order as those in the determination of As(III).

Remark

Fig. 2 illustrates the calculated inaccuracy of an As(V) determination as a function of the mol % As(V) in a mixture of As(III) and As(V) when the As(V) concentration is found as the difference of two As(III) determinations, one before and one after reduction, each with an inaccuracy of 2%.

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TABLE I

LIMITING CURRENT OF As(III)

No.	*As(III) conc.* $10^{-5}M$	$E_{\frac{1}{2}}$ *vs. S.C.E. volt*	i_d *found* μA	i_d *calculated** μA	Δ %
1	100	—0.66	26.00	25.68	+ 1.2
2	100	—0.66	25.50	25.68	— 0.7
3	100	—0.66	25.50	25.68	— 0.7
4	100	—0.66	25.50	25.68	— 0.7
5	50	—0.66	12.70	12.84	— 1.1
6	40	—0.66	10.60	10.27	+ 3.0
7	10	—0.66	2.56	2.57	— 0.3
8	10	—0.66	2.61	2.57	+ 1.6
9	4	—0.67	1.03	1.03	+ 0.3
10	1	—0.68	0.15	0.26	—40.0

* Calculated from the data in column 2 and 4 by the method of least squares.

TABLE II

REDUCTION OF As(V)

No.	*As(V) conc.** $10^{-5}M$	*HS conc. mg/100 ml*	H_2SO_4 *conc.* %	*Heating time min*	$E_{\frac{1}{2}}$ *vs. S.C.E. volt*	i_d *found* μA	*As(V) conc. calc. from* i_d $10^{-5}M$	Δ %
1	92	50	80	5	—0.66	21.6	84	— 9
2	92	50	80	5	—0.66	21.3	83	—10
3	92	50	80	5	—0.66	21.1	82	—11
4	92	50	80	30	—0.66	22.7	88	— 4.5
5	92	150	80	5	—0.66	20.5	80	—13
6	92	150	80	15	—0.66	21.6	84	— 9
7	92	150	80	30	—0.66	19.4	76	—17.5
8	92	100	80	10	—0.66	23.9	93	+ 1
9	37	100	80	10	—0.66	9.5	37	0
10	37	100	80	10	—0.64	9.6	37	0
11	37	100	80	10	—0.64	9.6	37	0
12	37	100	80	30	—0.64	9.5	37	0
13	92	100	80	30	—0.66	23.9	93	+ 1
14	92	100	70	10	—0.66	23.8	93	+ 1
15	92	100	55	10	—0.66	23.8	93	+ 1
16	92	100	45	10	—0.66	23.9	93	+ 1
17	92	100	35	10	—0.66	18.5	72	—22
18	92	100	30	10	—0.66	13.6	53	—45

* As(V) content of the stock solution determined by titration with $Na_2S_2O_3$ after addition of KI.

CONCLUSIONS

The polarographic determination of As(III) in $1N$ H_2SO_4 was found possible for concentrations between $10^{-3}M$ and $4.10^{-5}M$.

When tolerating a standard deviation of 1.5% no particular precautions are needed (Table I).

As(V) may be determined within the same concentration limits after reduction by hydrazine sulphate in sulphuric acid of at least 45% by heating at 180-200°C for ten minutes (Table II).

The successive polarographic analysis of As(III) and As(V) may be performed by the method given above. The standard deviation of the results obtained for the total

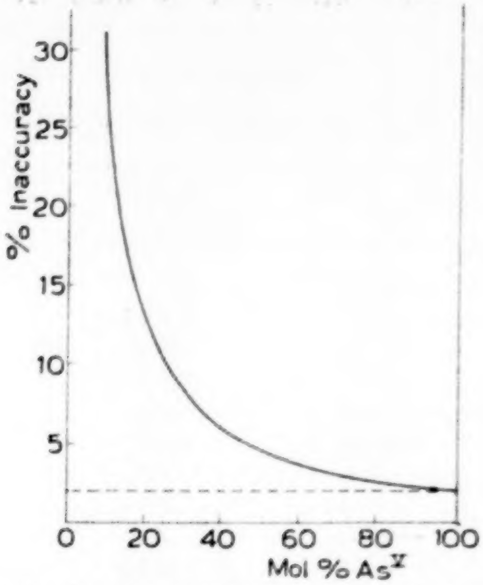

Fig. 2. Inaccuracy of As(V) determination in As(III) + As(V) mixture as a function of mol % As(V).

As content of the mixture is 1.8% (Table III). The inaccuracy in the As(V) content depends on the percentage As(V) of the mixture (Fig. 2).

The determination of both As(III) and As(V) in the same sample is not practical. After recording the polarogram of As(III) one has to acidify the solution strongly for the reduction of As(V), and afterwards to dilute it strongly in order to restore the medium to 1 *N*. This may imply an inadmissible decrease of the As concentration. Hence, we recommend separate determinations for As(III) and As(III) + As(V) according to the following procedure:

TABLE III

LIMITING CURRENT OF As(III) + As(V)

No.	*As(III)conc.* $10^{-5}M$	*As(V)conc.* $10^{-5}M$	*As(III)/As(V)*	*Total As(III) conc. after reduction* $10^{-5}M$	$E_{\frac{1}{2}}$ *vs. S.C.E. volt*	i_d *found* μA	*Total As(III) conc. calculated from* i_d $10^{-5}M$	Δ %
1	40	37.2	1:1	77.2	—0.67	20.0	77.8	+0.8
2	40	37.2	1:1	77.2	—0.65	19.8	77.1	—0.1
3	80	37.2	2:1	117.2	—0.66	31.6	119.2	+1.8
4	40	74.4	1:2	114.4	—0.67	30.4	118.4	+3.0
5	40	74.4	1:2	114.4	—0.66	30.3	118.0	+3.0
6	40	9.3	4:1	49.3	—0.66	13.0	50.6	+2.2
7	10	37.2	1:4	47.2	—0.66	12.3	47.9	+1.8
8	40	3.7	10:1	43.7	—0.66	11.2	43.7	0.0
9	40	3.7	10:1	43.7	—0.65	11.4	44.4	+1.1
10	100	9.3	10:1	109.3	—0.66	27.7	107.9	+1.0
11	10	93.0	1:10	103.0	—0.66	25.5	101.0	—2.0
12	10	93.0	1:10	103.0	—0.66	25.1	100.0	—3.0
13	4	37.2	1:10	41.2	—0.67	10.8	42.0	+1.9
14	4	37.2	1:10	41.2	—0.65	10.8	42.0	+1.9
15	100	7.4	13:1	107.4	—0.66	27.9	108.7	+1.2
16	8	93.0	1:12	101.0	—0.66	24.4	98.4	—2.5
17	100	3.7	25:1	103.7	—0.65	26.4	102.8	—0.9
18	100	3.7	25:1	103.7	—0.65	26.8	104.4	+0.7
19	4	93.0	1:25	97.0	—0.66	25.2	98.4	+1.5
20	4	93.0	1:25	97.0	—0.66	24.9	97.0	0.0

PROCEDURE

Add to a measured quantity of sample sulphuric acid and gelatin so that the concentrations are respectively between 10^{-3} and $5 \cdot 10^{-5} M$ for As(III), 1*N* in respect to H_2SO_4 and 0.01% by wt of gelatin. Record a polarogram and determine the limiting diffusion current of the wave with half-wave potential of —0,66 V *vs.* S.C.E. From this find the As(III) concentration by comparing with standard As(III) solutions.

Add to a second sample as much sulphuric acid and hydrazine sulphate as to obtain a solution of 80% H_2SO_4 with a total As concentration between 28,2 and 1,4 mM and a HS content of about 300 mg/10 ml; heat at 180—200°C for ten minutes. (Should it be difficult to obtain a H_2SO_4 conc. as high as 80%, it is allowed to lower this limit to 45%, provided that the As and HS concentrations are lowered correspondingly.) After cooling dilute to bring the H_2SO_4 concentration to 1*N*, add the required amount of gelatin and record a new polarogram. From this find the total As concentration as stated above for As(III).

ACKNOWLEDGEMENT

The authors wish to express their gratitude to Prof. J. SMITTENBERG for his aid in the preparation of this paper.

SUMMARY

A method has been described for the successive polarographic determination of As(III) and As(V) in a 1*N* sulphuric acid solution.

A directly recorded polarogram shows a limiting current corresponding to the As(III) concentration; another polarogram, recorded with a second sample after reduction of As(V) to As(III) by hydrazine sulphate, gives a limiting current corresponding to the concentration As(III) + As(V).

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REVUE DE LIVRES

Spot tests in organic analysis, par **Fritz Feigl**. Traduit par **Ralph E. Oesper**. Cinquième édition anglaise revue et augmentée. XX + 620 p. Elsevier Publishing Company, Amsterdam, 1956, £ 2.15.—.

M. Feigl, le pionnier de l'analyse à la touche, nous présente aujourd'hui, en cinquième édition, la partie organique de son livre bien connu "Spot tests". Déjà, lors de la quatrième édition, l'auteur s'est vu obligé de diviser son livre en deux volumes, le premier traitant les applications minérales et le second les applications organiques.

Les développements récents, réalisés principalement par l'auteur, dans le domaine de l'analyse organique ont rendu nécessaire une séparation complète du livre en deux parties indépendantes. Nous ne pouvons que saluer cette heureuse initiative de M. Feigl, car son livre tel qu'il est présenté aujourd'hui constitue un aide des plus précieux pour le chimiste qui s'occupe de l'analyse organique.

D'une façon générale, les réactions proposées sont simples et efficaces. Minutieusement étudiées par l'auteur lui-même elles sont exposées avec tous les détails nécessaires à leur application (mode opératoire précis, limites de sensibilité, interférences).

Le livre comprend tout d'abord une introduction générale aux réactions à la touche, puis un chapitre important consacré aux essais préliminaires (identification des éléments dont la substance à analyser est composée et quelques autres réactions ayant trait aux caractères généraux de la substance et servant à orienter la recherche ultérieure). Le chapitre suivant est consacré à l'analyse fonctionnelle (identification des groupements particuliers). Il suit un chapitre traitant l'identification de quelques produits organiques, parmi les plus courants et enfin l'auteur nous donne un très grand nombre d'exemples d'application pratique (colorants, produits pharmaceutiques et divers autres produits de l'industrie).

Tout cela est accompagné d'innombrables références bibliographiques et d'un tableau, à la fin du livre, résumant les principales réactions. Nous ne pouvons donc que recommander chaudement ce livre, tout spécialement aux chimistes qui s'occupent de l'analyse organique.

I. **Kapetanidis** (Genève)

Elementary quantitative analysis. – Theory and practice. W. J. **Blaedel et** V. W. **Meloche** – Row, Peterson and Company Evanston, Illinois, White Plains N. Y. 1957, 826 pp. $ 6.90.

Ce nouveau traité s'adresse particulièrement aux étudiants et à tous ceux qui veulent acquérir les bases théoriques et pratiques de la chimie analytique moderne. Tout est mis en oeuvre pour faciliter l'assimilation. On y trouve des exposés clairs et bien ordonnés où chaque fait nouveau est expliqué dans ses moindres détails. A la fin des chapitres, de nombreux problèmes et exercices d'application avec réponses complètent les explications qui sont d'autre part illustrées de tableaux et schémas fort suggestifs.

On y trouve aussi la description de nombreuses expériences minutieusement choisies du point de vue didactique.

La partie introductive comprend, entre autres, un chapitre sur la théorie des erreurs dans lequel le problème de la précision et de l'exactitude est largement développé.

Dans la seconde partie, les auteurs traitent de l'analyse gravimétrique. Ils y développent la partie technique, précipitation, filtration, dessication, calcination, etc. et en exposent les bases théoriques, telles que celles de la solubilité et de l'état colloïdal, de l'adsorption et de la contamination des précipités. L'analyse volumétrique est traitée dans la troisième partie. On y trouve la technique du dosage et les erreurs qui s'y rapportent. Les courbes de titrations, l'équilibre acide-base, red-ox. et les méthodes d'analyse basées sur ces deux phénomènes.

La quatrième partie est spécialement réservée à l'absorptiométrie, les auteurs traitent des méthodes colorimétriques, spectrophotométriques, de la chimie de l'absorption et terminent par un chapitre sur l'instrumentation en chimie analytique. Cette dernière partie est peu développée.

Pour qu'il n'y ait pas de confusion, les auteurs ont évité de surcharger certains chapitres. Dans un supplément qui termine ce traité, ils ont repris certains sujets importants pour leur donner plus d'ampleur. C'est ainsi que la question de l'erreur, de la balance, du mécanisme de la cristallisation et de la coagulation, la spectrophotométrie y trouvent un nouveau développement.

Un livre remarquable, bien présenté, très complet que nous recommandons vivement.

D. **Monnier** (Genève)

DETERMINATION OF HYDROGEN IN MAGNESIUM BY COMBUSTION

by

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INTRODUCTION

Hydrogen in magnesium causes microporosity[1,2], therefore its determination is a matter of importance. Commercial magnesium and magnesium alloys ordinarily contain 0.001 to 0.003% hydrogen. However, magnesium alloys containing up to 0.3% hydrogen have been prepared[3,4]. Hydrogen is present in magnesium and magnesium alloys in interstitial solid solution up to the extent of 15 to 20 cc of hydrogen per 100 g of metal (0.0013 to 0.0018%).

Hydrogen in magnesium cannot be determined by the regular vacuum fusion methods because the magnesium sublimes and re-absorbs the hydrogen[5]. Also, the sublimed magnesium reacts with the water vapor absorbed on the cooler parts of the apparatus to produce a spurious source of hydrogen[6]. The determination cannot be performed by hot vacuum extraction using a solid specimen, because hydrogen does not diffuse through solid magnesium[7].

The following methods have been used for the determination of hydrogen in magnesium:

1. Passing an inert gas (helium) through the molten metal and oxidizing the released hydrogen with copper oxide[8].
2. Vacuum extraction at about 700°C followed by resublimation of the condensed magnesium[8].
3. Vacuum extraction at about 800°C after sealing the specimen in a steel capsule[6].
4. Vacuum extraction after dissolving the magnesium in a molten tin bath[6].
5. Ionic bombardment by making the specimen the cathode in a vacuum discharge tube[8].
6. Treatment of the molten metal with a mixture of chlorine and oxygen. The hydrogen forms hydrogen chloride which is oxidized to water with copper oxide[9].
7. Combustion of the sample in oxygen to convert the hydrogen to water[8].

Of all the above methods the one that seemed most convenient for laboratories performing only an occasional analysis was Method 7, the combustion method. Therefore, an investigation was undertaken to refine that method. The following improvements were made:

1. The sample was placed in a large porcelain or alumina boat which was then inserted in a sillimanite protective tube. By this means up to a 15 g sample could be combusted. A 2 or 3 g sample had been used previously in determining hydrogen in magnesium by combustion[8].

2. The blank was reduced to 0.1 mg or less by using an all glass apparatus and preigniting the boats at 1100°C and storing them in a muffle at 500°C.

3. Argon was used together with the oxygen. This made possible controlled burning of the magnesium. It was found that more complete combustion of the magnesium was obtained if the flow rate of oxygen were about 250 ml/min rather than the 1000 ml or more per minute frequently used in combustion analyses. The reason for incomplete combustion at a high flow rate may lie in the fact that the intense heat of the rapid initial combustion can cause some of the magnesium to volatilize and burn above the boat, forming a crust that prevents ready access of oxygen to the interior of the boat. The fact that at high temperatures magnesium tends to volatilize and burn some distance away from the surface is well known[10]. Another purpose that the argon serves is that it prevents suck back of gases from the exit end of the system. This suck back of gases can produce a significant error because of hydrogen and hydrogen compounds present in the atmosphere. The free hydrogen content of the normal atmosphere is somewhat less than 1 part per million by volume[11]. However, it would be expected to be considerably more than this in many laboratories, because of electrolyses and the presence of unburnt illuminating gas (carbon monoxide and hydrogen). Certainly the amount of hydrogen compounds present in a laboratory atmosphere would be very significant. Such hydrogen compounds as water, hydrogen chloride and hydrogen sulfide would be removed by placing a column of anhydrone and ascarite at the end of the train. However, organic vapors and free hydrogen would not be so removed. The use of an inert gas (helium) to obtain controlled combustion was first suggested by KALLMANN[12] for the determination of hydrogen in titanium using lead as a flux.

4. Purification of the oxygen and argon by passing the gases through a 12 inch column of copper oxide heated to 800°C (followed by ascarite and anhydrone). This removes hydrogen compounds from the oxygen and argon, no matter what the flow rate and helps eliminate the random errors described by BOBALEK AND SHRADER[8].

APPARATUS

The apparatus is shown in Fig. 1. The furnaces were of the hinge type (70 and M2012, Central Scientific Co.). The boats were glazed porcelain (Coors, 100 mm in length, 13 mm in width and 10 mm in height), or alumina (Norton, 5 in. in length, 3/4 in. in width and 1/2 in. in height). The protective tubing was prepared by cutting 30 in. pieces of Coor sillimanite tubing (15/16 in. internal diameter, and 1 in. external diameter). All ground glass joints were held together by springs. When the absorption tube was not in use, it was protected from the atmosphere by means of a ground glass plug and a policeman. The reaction tube was protected by attaching a copper oxide tube filled with anhydrone.

PROCEDURE

If the reaction tube is new, heat it to 900–1000°C for 2 hours while passing a slow stream of oxygen through it. Ignite the protective tube and several boats in a muffle at 1100°C for 3 hours. Insert the protective tube into the reaction tube, and store the boats in a muffle at 500°C or above.

Prepare a sample with the approximate dimensions 9 cm × 1 cm × 1 cm. Such a specimen will weigh about 15 g. Remove the exterior surface by scraping with a clean wide file, while holding the sample in a vise and handling it with a cloth to prevent contact with the perspiration of the hands. Store the sample in a dessicator.

Heat the copper oxide in the purification train to about 800°C and the reaction tube to about 300°C while passing a stream of oxygen through the system (no argon). Place the weighed sample into an ignited boat, insert the boat into the protective tube and push the protective tube to the center of the reaction tube. Attach the copper oxide tube and heat it with the Meeker burner. Increase the flow of oxygen to about 250 ml/min and attach the absorption tube, suck back trap and bubbler.

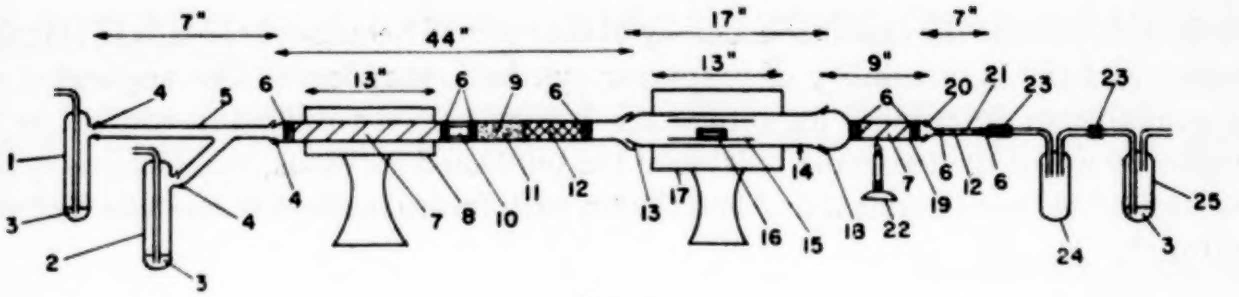

Fig. 1.

1. Bubbler for argon, 6 in. in height. 2. Bubbler for oxygen, 6 in, in height. 3. Sulfuric acid. 4. Ground glass joint (24/40). 5. Adapter, borosilicate glass, 18 mm in diameter. 6. Glass wool. 7. Copper oxide, fine wire form. 8. Electric heater, hinge type, 1¼ in. opening. 9. Copper oxide-ascarite-anhydrone tube, 96% silica, 25 mm in diameter. 10. Borosilicate glass tubing, 19 mm in diameter and 2 in. long, to separate ascarite from copper oxide. 11. Ascarite. 12. Anhydrone. 13. Ground glass joint (29/42). 14. Reaction tube, 96% silica, 38 mm in diameter. 15. Sillimanite protective tube, 10 in. in length. 16. Boat. 17. Electric heater, hinge type, 2 to 2½ in. opening. 18. Ground glass joint (40/50). 19. Copper oxide tube, 96% silica, 18 mm in diameter. 20. Ground glass joint (10/30). 21. Absorption tube, borosilicate glass, 8 mm in diameter. 22. Meeker burner. 23. Tygon tubing. 24. Suck-back trap, 4 in. in height. 25. Bubbler, 4 in. in height.

After 5 min detach the absorption tube and close its ends. Allow to stand for 15 min in the balance case, open to the atmosphere momentarily and weigh. Reattach the absorption bulb for 5 min more and weigh again to check for constant weight.

Turn on the argon and adjust its flow rate to about 100 ml per minute. Attach the absorption tube, and heat the reaction tube to about 700°C. The magnesium will ignite in a few minutes. Continue the flow of oxygen and argon until the burning is complete, meanwhile raising the temperature of the reaction tube to about 800°C. Shut off the argon and allow oxygen alone to flow through the system for 10 min. Detach the absorption bulb and weigh as above. Run a blank by proceeding as above without the sample.

Calculate the per cent hydrogen as follows:

$$\text{Per cent hydrogen} = \frac{11.2\,(A-B)}{W}$$

where:

A = weight of water (g)
B = weight of water in blank (g)
W = weight of sample (g)

To proceed with the next determination, open the heater and allow it to cool to about 300°C. Draw the protective tube towards the exit end of the reaction tube and remove the boat. Do not draw over the protective tube while it is still red hot, it may crack. If necessary scrape out the inside of the protective tube. Insert another boat containing a new sample and proceed as described above.

RESULTS

The results obtained for hydrogen when the two samples were run five times each are shown in Table I. One of the samples was commercial magnesium. The other sample was magnesium of low hydrogen content prepared by sublimation. The authors were

TABLE I

RESULTS FOR HYDROGEN (%)

Sample 1 (commercial magnesium)	*Sample 2 (sublimed magnesium)*
0.0020	0.0006
0.0017	0.0006
0.0018	0.0007
0.0020	0.0007
0.0021	0.0008

unable to determine the absolute accuracy of the method because of the lack of standard samples and the impossibility of preparing synthetic standards. The apparatus was not available to determine, for comparative purposes, the hydrogen content of the samples by use of the two most reliable of the published methods, the vacuum extraction method of Dow Chemical Co.[8] and the tin bath fusion method of Battelle Memorial Institute[6].

DISCUSSION

Removal of the exterior surface of the sample is essential, otherwise high results for hydrogen will be obtained due to a coating of magnesium hydroxide. The magnesium should be stored in a dessicator before and after the surface is cleaned. If it is exposed to moist air, not only can the coating of magnesium hydroxide form, but also the atomic hydrogen produced by the reaction of the magnesium and water, will diffuse into the magnesium and raise its hydrogen content.

The magnesium ignites before it melts. The ignition temperature of magnesium is about 625°C[13] while its melting point is 650°C.

When porcelain boats were used, no blank at all was obtained. When alumina boats were used, a blank of 0.1 mg was obtained. Porcelain boats are slightly attacked and can be used only once. Alumina boats are practically unattacked and can be used again after re-ignition. Boats made from clay are unsatisfactory since they are so badly attacked (with the formation of black aluminum magnesium silicate) that the melt cracks the reaction tube. Boats made from magnesia might be ideal, but it is difficult to fabricate such boats. The boats must be stored in a muffle at 500°C as described. If they are stored in a desiccator, they will pick up moisture, particularly the alumina boats.

If desired, the carbon content of the magnesium can be determined at the same time as the hydrogen, by placing a tube containing manganese dioxide and anhydrone after the water absorption tube and then attaching a carbon dioxide tube containing ascarite and anhydrone. The manganese dioxide serves the purpose of absorbing oxides of sulfur and oxides of nitrogen[14]. The determination of carbon in magnesium is seldom required.

SUMMARY

The difficulties of determining hydrogen in magnesium are discussed. An improved combustion method is proposed. An all glass apparatus is used to reduce the blank to 0.1 mg or less. Up to a 15 g sample can be combusted by placing the sample in a large porcelain or alumina boat which is then inserted in a sillimanite protective tube. Argon is used to control the combustion and prevent suck back of gases from the laboratory atmosphere, which frequently contains hydrogen and hydrogen compounds. It is essential that the boats be pre-ignited at 1100°C and stored in a muffle at 500°C.

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THE Fe(II) AND Co(II) CHELATION COMPLEXES OF 2,6-BIS(4-ETHYL-2-PYRIDYL)-4-PHENYL-PYRIDINE

by

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INTRODUCTION

Substitutions of the three replaceable hydrogens in the 4,4′- and 4″-positions in 2,2′,2″-terpyridine alter the chelation reaction of the modified molecule to a high degree in the formation of both complexes with Fe(II) and Co(II). Previously described modified terpyridines are the following:

2,6-bis(2-pyridyl)-4-phenyl-pyridine: "Terosine".
2,6-bis(4-methyl-2-pyridyl)-4-phenyl-pyridine: "Terosole".
2,6-bis(4-phenyl-2-pyridyl)-4-phenyl-pyridine: "Terosite".

Together with terpyridine (2,2′,2″-tripyridine), the molecular extinction coefficients of the substituted terpyridines as their Fe(II) complex cations are, in the order given above, 22,000, 26,300 and 30,200 at wave lengths of maximum absorption 569, 575, and 583 mμ as compared to 12,500 at wave length 522 mμ for the unsubstituted terpyridine. These 4 ligands do not form colored Cu(I) complexes in the visual range of the spectrum. All form Co(II) colored complexes with rather low (2,710 to 3,120), molecular extinction coefficients.

The effect of the substitution of methyl groups in the 4,4′-positions of dipyridine and in the 3- to 8-positions in 1,10-phenanthrolines is that of an increase in both extinction coefficients and wave lengths of maximum absorption in their Fe(II) complex cations. The substitution of ethyl groups for methyl groups has a noticeable increase in the same organic chelation reagents, as compared to methyl group substitutions.

It is the object of the present work to describe the substitution of ethyl groups for the methyl groups in the case of "terosole" in the compound named in the title of this communication, to which the trivial name "ethyl-terosole" is applied.

EXPERIMENTAL

Preparation of 2,6-bis(4-ethyl-2-pyridyl)-4-phenyl-pyridine

This new modified terpyridine was synthesized by CASE AND KASPER at Temple University in Philadelphia and a detailed description of the procedure will appear elsewhere in association with comparable types to be described.

Properties. This reagent is soluble in chloroform and ethanol-hydrochloric acid solutions. A 0.010*M* solution was prepared by dissolving the material in 95% ethanol to which was added, dropwise, enough reagent grade hydrochloric acid to make a clear solution.

All attempts to form a colored copper(I) complex failed.

This chelation reagent reacts with Fe(II) to give a purple-colored complex which is insoluble in aqueous solutions but soluble in aqueous ethanolic solutions. The purple complex may be quantitatively extracted with chloroform over the pH range 1.0 to 12 (two extractions are requisite), 96.8% complete in one extraction.

Preparation of the complex with Fe(II) for spectroscopic examination

The spectrophotometric absorption of this Fe(II) complex is shown in Fig. 1. The wave length of maximum absorption in the visual range is at 570 mμ. The absorption is also indicated to be high in the near U.V. range.

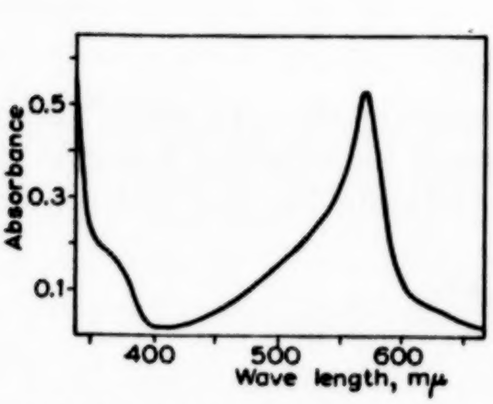

Fig. 1. Ethyl-terosole-Fe(II)-complex spectrophotometric absorption curve.

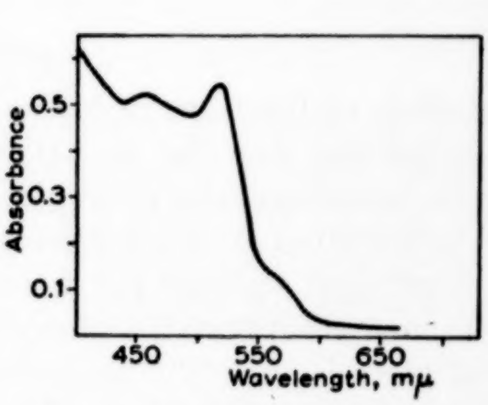

Fig. 2. Ethyl-terosole-Co(II)-complex spectrophotometric absorption curve.

For the determination of the molecular extinction coefficient, weighed amounts of standard iron solution (0.1108 mg of Fe per g), were transferred to 25 ml glass stoppered volumetric flasks containing 5.0 ml of buffer solution of pH 4.0, 1 ml of reagent solution and 2 ml of 10% aqueous hydroxylamine hydrochloride. The contents of the flasks were diluted to volume with 95% ethanol. Spectrophotometric evaluations were made employing a Cary Recording instrument, Model 14M, using 10 mm silica cells. An appropriately prepared blank solution was used in the reference cell.

The results are given in Table I. Solutions of the complex were stable in storage in the stoppered flasks for an interval of 30 days by test.

By examination of the data of Table I it will be observed that the molecular extinction coefficient of the Fe(II) complex of ethyl-terosole is greater by approximately 3% than that of its methyl-substituted analogue. The sensitivity of this newly modi-

TABLE I

SPECTROPHOTOMETRIC DATA IN THE DETERMINATION OF THE MOLECULAR EXTINCTION COEFFICIENT OF THE Fe(II) COMPLEX OF 2,6-BIS(4-ETHYL-2-PYRIDYL)-4-PHENYL-PYRIDINE (TRIVIAL NAME "ETHYL-TEROSOLE")

Wt. Fe soln. g	*Wt. Fe taken* mg	*Absorbance at 570 mμ*	*Molar absorptivity at 570 mμ*
0.348	0.0386	0.748	27,100
0.493	0.0546	1.060	27,070
0.554	0.0614	1.194	27,180
0.639	0.0708	1.372	27,050
			Av. 27,100

fied terpyridine is second only in value to the comparable terosite complex (mol. extinction coefficient 30,200). The modifying effect of the substitution of the ethyl group for the methyl group in the terpyridine types has somewhat lesser effect on properties than such substitutions in similar positions in 1,10-phenanthrolines and dipyridines.

Ethyl-terosole in chelation with Co(II)

This cobalt chelation complex is formed under the same conditions as that described for the Fe(II) complex stable over the pH range 3.1 to 8.8. By following the same procedure as that described in the case of iron chelation except that a cobalt solution containing 0.1179 mg of cobalt per g of solution as nitrate was used, the Co(II) complex may be formed.

The spectrophotometric absorption characteristics of the ethyl-terosole in the visual range are given in Fig. 2.

The data obtained in the calculation of the molecular extinction coefficient of the ethyl-terosole Co(II) complex are given in Table II.

TABLE II

THE SPECTROPHOTOMETRIC DETERMINATION OF THE MOLECULAR EXTINCTION COEFFICIENT OF THE Co(II) COMPLEX OF ETHYL-TEROSOLE

Cobalt soln. g	*Absorbance*		*Molar absorptivity*	
	456 mμ	*517 mμ*	*456 mμ*	*517 mμ*
0.873	0.179	0.185	2,560	2,650
1.891	0.395	0.411	2,610	2,710
2.491	0.523	0.543	2,620	2.730
2.951	0.618	0.644	2.620	2.720
3.536	0.747	0.778	2.640	2.710
			Av. 2.610	2.710

SUMMARY

A study has been made of the spectrophotometric constants of the new modified terpyridine chelation reagent, 2,6-bis(4-ethyl-2-pyridyl)-4-phenyl-pyridine (trivial name "ethyl-terosole"), as its Fe(II) and Co(II) complex cations. This new ligand is outstanding for use in the trace quantity determination of iron. No advantage as compared to more sensitive ligands previously studied is provided by Co(II) chelation.

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DÉVELOPPEMENT PAR DÉPLACEMENT SUR ÉCHANGEURS D'IONS. CAS DE LA SÉPARATION DE DEUX IONS

par

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Le principe de la méthode du développement ou de l'analyse par déplacement, imaginée per TISELIUS[1], est le suivant: on fixe à la partie supérieure d'une colonne pour chromatographie une certaine quantité de solutés à séparer. On introduit ensuite une solution d'un corps, appelé développeur, ayant plus d'affinité que les précédents pour la phase immobile. Ce développeur agit comme une sorte de piston[2] qui pousse les différents solutés. A leur tour, ces ions déplaceront l'ion initialement contenu dans la résine, à condition que ce dernier ait encore moins d'affinité pour la résine. De cette manière, on obtient une bande qui migre le long de la colonne.

Après un certain parcours, les solutés sont répartis dans cette bande en différentes zones jointives, dans l'ordre de leur affinité croissante pour la phase fixe.

Ces zones, une fois formées, sont stables et ne se détruisent pas au cours d'une migration ultérieure de la bande initiale.

Autrement dit, un état de régime dynamique est obtenu après un certain parcours.

Cette méthode, qui présente un grand intérêt en chimie préparative[3], a permis de résoudre un certain nombre de problèmes dans le domaine de la biochimie**: séparation d'acides gras[2], d'acides aminés[4], de protéines[5], de lipides[6] par chromatographie d'adsorption et d'acides aminés[7] au moyen de résines échangeuses d'ions.

En ce qui concerne la chimie minérale, la méthode par déplacement a été employée avec les échangeurs d'ions pour séparer les terres rares[2], les isotopes de l'azote[9] et du calcium[10].

Dans le cas de la chromatographie d'adsorption, TISELIUS[1] a initialement montré qu'il était possible de prévoir les concentrations des solutés dans chacune des zones, une fois celles-ci formées, à l'aide de la connaissance des isothermes d'adsorption des différents solutés et du développeur. Ce problème de la répartition des corps à l'état de régime, a été repris par différents auteurs en ce qui concerne la chromatographie d'adsorption[2,11], de partage[12,13] et d'échange d'ions[8,9,14].

Excepté SPEDDING et ses collaborateurs[9], aucun auteur n'a essayé de prévoir la distance à faire parcourir à la bande pour que celle-ci soit divisée en zones. Ce problème est important, car une fois l'état de régime établi, une migration ultérieure de la bande n'améliorant pas la séparation, il est inutile de poursuivre le développement de la bande. Autrement dit, la connaissance de la distance à faire parcourir à la bande permet de calculer la hauteur de colonne nécessaire pour effectuer la séparation ainsi que la quantité de développeur à utiliser et le temps de l'opération. Pour calculer cette distance, il faut connaître la manière dont les solutés se répartissent dans la bande au cours de la migration de cette dernière. Au début de l'opération, lorsqu'on fixe les corps à séparer sur la colonne, un enrichissement se produit au front de la bande, l'ion ayant le moins d'affinité pour la résine avançant plus vite que les autres.

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** Nous n'indiquons que quelques références récentes des principales écoles ayant utilisé cette méthode.

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Lorsque la bande est fixée et que l'on introduit le développeur, en tête de bande l'enrichissement augmente toujours comme dans le cas de l'analyse frontale, tandis qu'un enrichissement symétrique s'effectue en queue de bande. Nous avons donc cherché à prévoir les phénomènes au cours de l'analyse frontale proprement dite, dans le cas des échangeurs d'ions. Nous nous sommes proposés dans le cas de deux et de trois ions de prévoir à partir des constantes d'équilibre les volumes de rétention, c'est-à-dire les volumes d'effluent (solution sortant de la colonne) pour lesquels apparaissent un ou plusieurs solutés, la colonne contenant l'unité de masse de résine.

I. ÉQUILIBRE DE DEUX IONS ENTRE UNE RÉSINE ET UNE SOLUTION

Considérons une résine sulfonique et une solution aqueuse entre lesquelles se répartissent deux cations M_1 et M_2 selon l'équilibre:

$$\underset{\text{résine}}{M_1} + \underset{\text{eau}}{M_2} \rightleftarrows \underset{\text{résine}}{M_2} + \underset{\text{eau}}{M_1}.$$

Nous cherchons à exprimer les concentrations à l'équilibre des ions M_1 et M_2 dans l'une des phases en fonction des concentrations dans l'autre phase.

Nous appellerons C_1, C_{1R}, C_2 et C_{2R} les concentrations de M_1 et M_2 en solution aqueuse et dans la résine à l'équilibre, C_0 la concentration ionique totale en solution et C_R la capacité de la résine. Les concentrations dans la solution sont exprimées en équivalents/litre et dans la résine en équivalents/kg.

On dispose de trois relations:

Les bilans des cations dans chacune des deux phases:

$$C_1 + C_2 = C_0$$
$$C_{1R} + C_{2R} = C_R$$

La loi d'action de masses appliquée à l'équilibre précédent:

$$\frac{C_{2R} \cdot C_1}{C_{1R} \cdot C_2} = \frac{K_2}{K_1} = K$$

K_1 et K_2 représentent les constantes d'équilibre des ions M_1 et M_2 avec un troisième ion, d'ailleurs quelconque.

A l'aide des trois relations précédentes, on calcule:

$$C_{1R} = \frac{K_1 \cdot C_R \cdot C_1}{K_1C_1 + K_2C_2} = \frac{C_R \cdot C_1}{C_1 + K\,C_2} \quad \ldots\ldots\ldots\ldots \quad (1)$$

$$C_{2R} = \frac{K_2 \cdot C_R \cdot C_2}{K_1C_1 + K_2C_2} = \frac{K \cdot C_R \cdot C_2}{C_1 + K\,C_2} \quad \ldots\ldots\ldots\ldots \quad (2)$$

$$C_1 = \frac{K_2 \,.\, C_0 \,.\, C_{1R}}{K_2\, C_{1R} + K_1\, C_{2R}} = \frac{K \,.\, C_0 \,.\, C_{1R}}{K\, C_{1R} + C_{2R}} \qquad (3)$$

$$C_2 = \frac{K_1 \,.\, C_0 \,.\, C_{2R}}{K_2\, C_{1R} + K_1\, C_{2R}} = \frac{C_0 \,.\, C_{2R}}{K\, C_{1R} + C_{2R}} \qquad (4)$$

Remarque 1. La loi d'action de masses telle qu'elle est écrite ci-dessus suppose les coefficients d'activité des ions constants. Cette hypothèse est valable en première approximation dans le cas de l'analyse frontale car la concentration ionique totale (c'est-à-dire la force ionique) de la solution aqueuse est constante. K est une constante apparente, qui est, en particulier, une fonction de C_0.

Remarque 2. Lorsqu'on écrit que la concentration ionique totale est constante dans la résine, on suppose que les anions ne diffusent pas dans la résine (équilibre de DONNAN) ce qui est vrai en première approximation en solution pas trop concentrée.

II. ANALYSE FRONTALE – CAS DE DEUX IONS

Lorsqu'on introduit une solution contenant un ou plusieurs ions dans une colonne remplie de résine, ces ions se fixent sur la résine et leurs concentrations en solution diminuent. Cette nouvelle solution va à nouveau se mettre en équilibre avec une portion inférieure de résine, ce qui provoquera un nouvel appauvrissement de la solution. Ce phénomène est répété un grand nombre de fois au fur et à mesure de l'introduction de la solution influente. Les concentrations des ions en solution vont donc varier de leurs valeurs initiales jusqu'à zéro sur une certaine longueur de colonne. Dans tout ce qui suit nous supposerons cette longueur négligeable vis-à-vis de la longueur de la colonne, ce qui est vrai lorsqu'on à affaire à des corps dont les propriétés sont suffisamment différentes. Nous supposerons, de plus les phénomènes de diffusion et de convection négligeables.

Le volume de rétention d'un ion peut être prévu en faisant le raisonnement suivant: Supposons qu'à la partie supérieure d'une colonne, on introduise une solution contenant M_1 et M_2 aux concentrations C_1 et C_2 d'une façon continue, la résine contenant initialement ces ions aux concentrations C_{1R} et C_{2R}. A la partie supérieure de la colonne, la résine va être en équilibre avec une telle solution, puisque nous admettons que la composition de cette dernière ne change pas. Les concentrations des ions dans la résine sont donc calculées à l'aide des relations (1) et (2). De la même façon, à la partie inférieure de la colonne la solution sortante vient d'être en contact avec la résine sous sa forme initiale. La composition de l'effluent peut donc être calculée, avec les mêmes hypothèses, à l'aide des relations (3) et (4), C_{1R} et C_{2R} représentant les concentrations initiales des ions M_1 et M_2 dans la résine. Nous connaissons donc ainsi, l'état initial et l'état final de la colonne.

Pour calculer le volume de rétention d'un ion (volume écoulé à travers l'unité de masse de résine avant que cet ion n'apparaisse à sa concentration initiale), il suffit d'écrire le bilan de cet ion: la quantité introduite diminuée de celle écoulée est égale à la quantité fixée.

Considérons alors une colonne constituée de m g de résine pour laquelle M_2 a plus d'affinité que M_1. Supposons en outre qu'initialement il y a dans la colonne un défaut de M_2 vis-à-vis de sa concentration finale. Cet ion apparaîtra dans l'effluent lorsqu'un volume v défini par

$$v\,(C_2 - C_2') = m\,(C_2'R - C_2R)$$

sera passé à travers la colonne. Les concentrations C_2' et $C_2'R$ étant calculées respectivement à l'aide des relations (4) et (2). On en déduit le volume de rétention x de M_2:

$$x = \frac{V}{m} = \frac{C_2R + K\,C_1R}{C_1 + K\,C_2} = \frac{K_1\,C_2R + K_2\,C_1R}{K_1\,C_1 + K_2\,C_2} \quad \ldots\ldots\ldots \quad (5)$$

Cette relation générale est applicable aux cas où un seul des deux ions est présent dans l'une ou l'autre phase. Il suffit d'annuler la concentration de l'ion inexistant. En particulier si la résine est initialement sous forme M_1 et si l'influent est constitué par une solution de M_2 pur, il vient:

$$x = \frac{C_1R}{C_2} = \frac{CR}{C_0} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

Les formules simplifiées ainsi obtenues peuvent être établies directement par un raisonnement analogue à celui fait précédemment.

Les isoplanes d'absorption théoriques (courbes représentant les variations des concentrations dans l'effluent en fonction du volume écoulé) correspondant aux quatre cas possibles sont représentées Fig. 1.

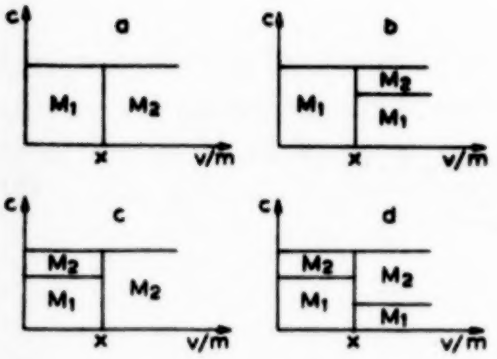

Fig. 1. Analyse frontale – cas de deux ions.

	Résine	Solution
a.	M_1	M_2
b.	M_1	$M_1 + M_2$
c.	$M_1 + M_2$	M_2
d.	$M_1 + M_2$	$M_1 + M_2$

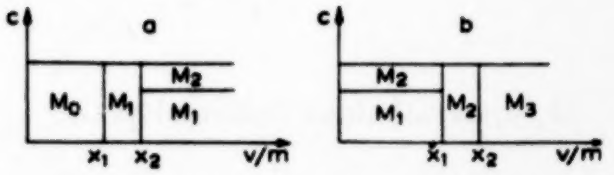

Fig. 2. Analyse frontale – cas de trois ions.

	Résine	Solution
a.	M_0	$M_1 + M_2$
b.	$M_1 + M_2$	M_3

III. ANALYSE FRONTALE – CAS DE TROIS IONS

Soient les quatre ions M_0, M_1, M_2, M_3 dont l'affinité pour la résine est dans l'ordre:

$$M_0 < M_1 < M_2 < M_3$$

Nous limiterons le problème au cas de la fixation des ions M_1 et M_2 sur une résine M_0 et à la sortie de M_1 et M_2 fixés sur la résine par une solution de M_3.

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1. Résine M_0 — solution $M_1 + M_2$

Puisque M_2 se fixe mieux que M_1, il y aura au front de la bande un excès de M_1. Celui-ci va déplacer quantitativement M_0, d'après ce qui a été dit précédemment, et au début l'effluent sera constitué par M_0 pur à la concentration $C_0 = C_1 + C_2$. Ensuite apparaîtra M_1 pur, puis le mélange initial.

Le volume de rétention x_1 de M_1 est donc d'après (6)

$$x_1 = \frac{C_R}{C_0}$$

M_2 apparaîtra pour un volume x_2 tel que:

$$C_{2R} = x_2 C_2$$

C_{2R} étant calculé à l'aide de la relation (2), soit:

$$x_2 = \frac{K\, C_R}{C_1 + K\, C_2} = \frac{K_2 C_R}{K_1\, C_1 + K_2\, C_2} \quad \ldots\ldots\ldots\ldots \quad (7)$$

2. Résine $M_1 + M_2$ — solution M_3

Les premières fractions sortantes sont en équilibre avec la résine. L'effluent est donc constitué par le mélange des deux solutés, plus riche en M_1 que la résine initiale. Il restera en queue une bande M_2 pur poussé par M_3, à la concentration C_0.

Il ne restera plus de soluté M_1 dans la résine lorsque:

$$x_1 C_1 = C_{1R}$$

C_1 étant calculée à l'aide de (3), soit:

$$x_1 = \frac{C_{2R} + K\, C_{1R}}{K\, C_0} = \frac{K_1\, C_{2R} + K_2\, C_{1R}}{K_2\, C_0} \quad \ldots\ldots\ldots\ldots \quad (8)$$

M_3 apparaît dans l'effluent pour:

$$x_2 = \frac{C_R}{C_0} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

Les isoplanes correspondant à ces deux cas sont représentées Fig. 2.

IV. DÉVELOPPEMENT PAR DÉPLACEMENT

Sur une résine M_0, on fixe une bande de $M_1 + M_2$ de longueur l_0 que l'on pousse par M_3. Au cours de la migration de la bande, les ions M_1 et M_3 sont fixés sur la résine à la partie inférieure de la bande tandis qu'ils repassent en solution à la partie supérieure. Le phénomène est donc la superposition des deux processus envisagés précédemment au § III, ceux-ci ayant lieu simultanément. Les isoplanes représentées Fig. 2 sont des images du profil de la bande.

Sur la Fig. 2a, la différence x_2—x_1 est proportionnelle à la longueur de bande l_1 contenant M_1 pur, tandis que x_2 est proportionnel à la distance L parcourue par la bande. Des relations (6) et (7) on déduit:

$$\frac{l_1}{L} = \frac{x_2 - x_1}{x_2} = \frac{K_2 - K_1}{K_2} \times \frac{C_1}{C_0} \quad \text{(10)}$$

De même, sur la Fig. 2b, la différence x_2—x_1 est proportionnelle à la longueur de bande l_2 contenant M_2 pur, tandis que x_1 est proportionnel au chemin L parcouru par la bande. Cette distance L est bien liée à x_1 et non à x_2, car il n'y a pas d'enrichissement pendant la parcours correspondant à la différence x_2—x_1 puisque tout le cation M_1 est déjà sorti de la colonne.

Des relations (8) et (9) on déduit:

$$\frac{x_2 - x_1}{x_1} = \frac{(K_2 - K_1)\, C_{2R}}{K_1 C_{2R} + K_2 C_{1R}}$$

soit:

$$\frac{l_2}{L} = \frac{x_2 - x_1}{x_1} = \frac{K_2 - K_1}{K_1} \times \frac{C_2}{C_0} \quad \text{(11)}$$

D'autre part, lorsque la bande aura atteint son état de régime, c'est-à-dire sera constituée de deux bandes de M_1 et M_2 purs, les longueurs des fractions contenant M_1 et M_2 seront respectivement égales à

$$l_1 = l_0 \frac{C_1}{C_0} \text{ et } l_2 = l_0 \frac{C_2}{C_0}$$

l_0 représentant la longueur totale de la bande. En remplaçant l_1 et l_2 dans les relations (10) et (11) par les valeurs précédentes, on en déduit les distances L_1 et L_2 à parcourir pour obtenir M_1 et M_2 purs:

$$L_1 = l_0 \frac{K_2}{K_2 - K_1}$$

$$L_2 = l_0 \frac{K_1}{K_2 - K_1}$$

On déduit de ces deux relations:

$$L_1 = L_2 + l_0$$

L'état de régime étant obtenu à un instant unique, puisqu'il n'y a que deux corps, il est naturel que le front de la bande ait parcouru une distance supérieure de l_0 au chemin effectué par la queue. En définitive, l'état de régime est atteint lorsque le front de la bande a parcouru une distance L tel que:

$$L = l_0 \frac{K_2}{K_2 - K_1} = l_0 \frac{K}{K - 1} \quad \text{(12)}$$

cette distance étant mesurée à partir du sommet de la colonne. Elle est d'ailleurs indépendante des proportions initiales des solutés. Elle ne dépend que de la constante de l'équilibre existant entre les deux ions.

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Remarque 1. Dans le cas de la séparation de deux isotopes, la constante K est égale à $1 + \varepsilon$. La formule (12) devient alors, en négligeant ε devant l'unité: $L = l_0/\varepsilon$. Cette relation a déjà été établie par SPEDDING et ses collaborateurs[9] au sujet de la séparation des isotopes de l'azote

Remarque 2. D'après le raisonnement précédent, tant que la bande n'a pas atteint son état de régime, elle est constituée de 3 zones: M_1 pur, mélange $M_1 + M_2$ dans les proportions initiales, M_2 pur. Ce fait a déjà été observé expérimentalement par les auteurs précités.

Remarque 3. Pratiquement, les zones de séparation entre les différentes bandes ne sont pas abruptes à cause des vitesses d'établissement des équilibres, de la grosseur des grains de résine, des phénomènes de diffusion, etc. . . . Enfin indépendamment les phénomènes précédents, les constantes d'équilibres n'étant jamais infinies, les équilibres ne sont pas quantitativement déplacés dans un sens donné et les variations des concentrations dans la bande se font d'une façon continue sur une certaine longueur de colonne. Comme l'a proposé MARTIN[13] dans le cas de la chromatographie de partage et comme l'ont vérifié les auteurs précédents, la théorie des plateaux rend compte de la forme des fronts. Lorsque les corps ont des propriétés suffisamment différentes, ces phénomènes peuvent être négligés en première approximation.

V. CONDITIONS OPÉRATOIRES

Nous avons cherché à vérifier les résultats théoriques précédents en utilisant de la résine Dowex-50, X-12, 200–400 mesh, les ions H^+, Na^+, K^+ et Ca^{+2} jouant le rôle des ions M_0, M_1, M_2 et M_3.

1. Détermination des constantes d'équilibre

1 g de résine sèche sous forme H^+ après avoir été humidifiée et gonflée est équilibré avec 10 ml d'une solution de chlorure de sodium ou de potassium 0.266*M*. A l'équilibre, on dose les ions H^+ en solution par acidimétrie.

La capacité de la résine est déterminée par dosage au moyen de soude titrée de 1 g de résine sèche sous forme H^+. Elle est égale à 5 millieq./g.

Les essais ont été effectués à l'aide de colonnes d'environ 10 cm de longueur et 1 cm² de section. Les débits sont de 0.4 – 0.5 ml/minute. Pour effectuer le calcul des volumes de rétention, il faut déduire du volume mesuré le volume interstitiel (volume de solution contenu dans la colonne) de la colonne, celle-ci étant initialement pleine d'eau. Ce volume a été déterminé expérimentalement. Il est égal à 4 ml (volume interstitiel + volume mort à la partie inférieure de la colonne).

Or, pour toutes les isoplanes tracées expérimentalement, les concentrations diffèrent de zéro à partir d'un volume égal à 10 ml. Nous pensons que l'écart de 6 ml correspond à une fixation d'ions sur la résine par équilibre de DONNAN. Comme on opère avec des solutions environ 0.25*N*, ces 6 ml correspondent à 1.5 milli-équivalent. La capacité totale des colonnes étant voisine de 30 milli-équivalents, l'hypothèse précédente semble être justifiée. De toute manière, aux volumes expérimentaux, on a retranché 10 ml afin d'obtenir le volume vrai.

La capacité totale des colonnes est déterminée en déplaçant les ions H^+ de la résine par une solution de chlorure de sodium ou de potassium et en dosant l'acidité totale de l'effluent.

Les essais relatifs à deux ions ont été effectués avec des solutions d'acide chlorhydrique et de chlorure de sodium. Seul H^+ est dosé par acidimétrie dans l'effluent, Na^+ est obtenu par différence.

Les essais relatifs à trois ions ont été également effectués en milieu chlorhydrique. Dans l'effluent, H^+ est titré acidimétriquement, les ions Na^+, K^+ et Ca^{+2} sont dosés à l'aide d'un photomètre à flamme Evans. La précision est de 5 à 10 % selon la concentration.

VI. RÉSULTATS EXPÉRIMENTAUX

1. Constantes d'équilibre

La constante de l'équilibre Na^+/H^+ est égale à 1.35, et celle relative à l'équilibre K^+/H^+ a pour valeur 2.35. Ces valeurs sont définies à ± 0.05 unité près.

La constante de l'équilibre K^+/Na^+ est égale au rapport des deux précédentes ce qui donne 1.75 comme valeur numérique.

2. *Analyse frontale-cas de deux ions*

Les résultats sont rassemblés dans le Tableau I. Les volumes théoriques sont calculés à l'aide de la relation (5) en prenant $K = 1.35$. Les isoplanes relatives aux essais No. 1 et 5 sont représentées Fig. 3 et 4.

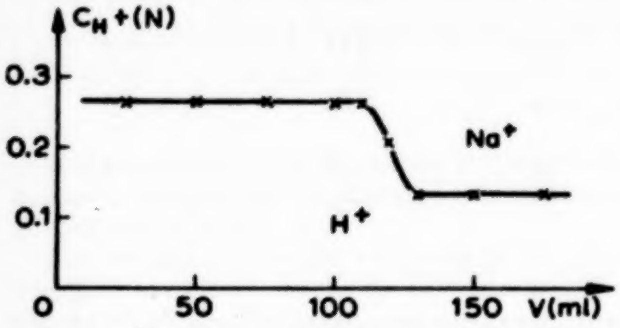

Fig. 3.

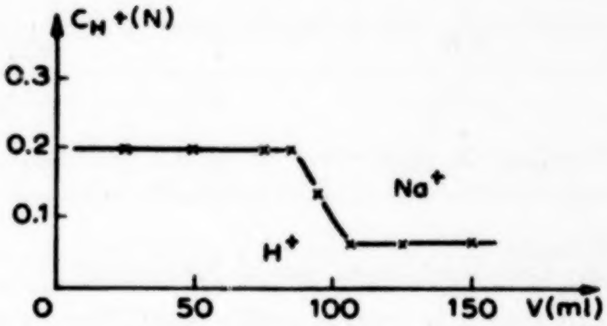

Fig. 4.

TABLEAU I

Opération	*No. de l'essai*	*Concentrations initiales Eau: équivalent/litre Résine: équivalent/kg*				*Volume de l'effluent (ml)*	
		NaCl	*HCl*	*NaR*	*HR*	*Expérimental*	*Calculé*
HR + (HCl + NaCl)	1	0.133	0.133	0	5	110	114
	2	0.066	0.200	0	5	139	136
	3	0.200	0.066	0	5	105	106
(HR + NaR) + NaCl	4	0.266	0	1.56	3.44	76	81
(HR + NaR) + (HCl + NaCl)	5	0.200	0.066	1.56	3.44	85	87

3. *Analyse frontale-cas de trois ions*

Sur une résine H^+ on introduit une solution de chlorure de sodium et de potassium $0.133M$ — une fois toute la résine transformée, les ions alcalins sont déplacées avec une solution de chlorure de calcium également $0.133M$.

Les résultats sont rassemblés dans le Tableau II. Les volumes théoriques sont calculés à l'aide des relations (6) à (9), les capacités totales des colonnes ayant été préalablement déterminées.

Les isoplanes correspondant aux essais 7 et 8 sont représentées Fig. 5 et 6.

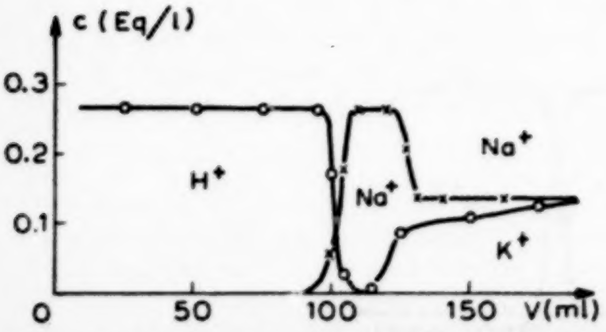

Fig. 5. Variation des concentrations dans l'effluent. (Résine H^+ — Solution de chlorure de sodium et de potassium $0.133M$).

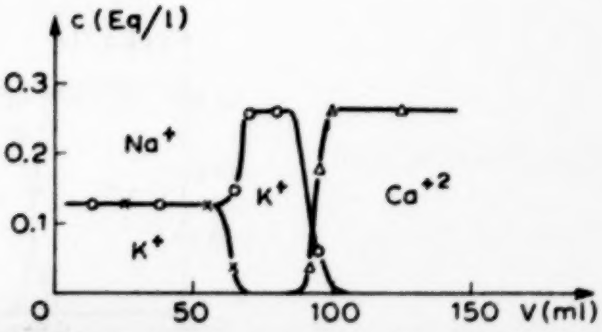

Fig. 6. Variation des concentrations dans l'effluent. (Résine Na^+ (1.82) et K^+ (3.18) — Solution de chlorure de calcium $0.133M$).

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TABLEAU II

Opération	*No. de l'essai*	*V₁ (ml)*		*V₂ (ml)*	
		Calculé	*Expérimental*	*Calculé*	*Expérimental*
(NaCl + KCl) + HR	6	99	101	128	132
	7	93	93	121	117
$CaCl_2$ + (NaR + KR)	8	58	54	82	85
	9	56	54	77	77

4. *Développement par déplacement*

On fixe à la partie supérieure d'une colonne une certaine quantité d'ions Na^+ et K^+ que l'on déplace ensuite avec une solution de chlorure de calcium. Les ions sodium et potassium doivent être séparés lorsque la bande aura parcourue un chemin égal à

$$\frac{2.35}{2.35-1.35} = 2.35 \text{ fois sa longueur d'après la relation (12).}$$

Au lieu d'utiliser des colonnes de longueurs différentes, nous avons préféré prendre une colonne de 30 cm de hauteur et effectuer le développement de bandes de longueur variable.

Sur les Figs. 7, 8 et 9 les concentrations des différents ions sont représentées en fonction du volume de l'effluent pour des bandes contenant initialement une même concentration de sodium et de potassium. Le développeur est constitué par une solution de chlorure de calcium $0.133M$ dans les deux premiers cas et $0.160M$ pour les courbes représentées Fig. 9. Ces bandes ont respectivement pour longueur 19, 15 et 10 cm. Elles ont donc parcouru 1, 6, 2 et 3 fois leur longueur. La séparation est complète seulement dans le dernier cas, ce qui est en accord avec les résultats précédents.

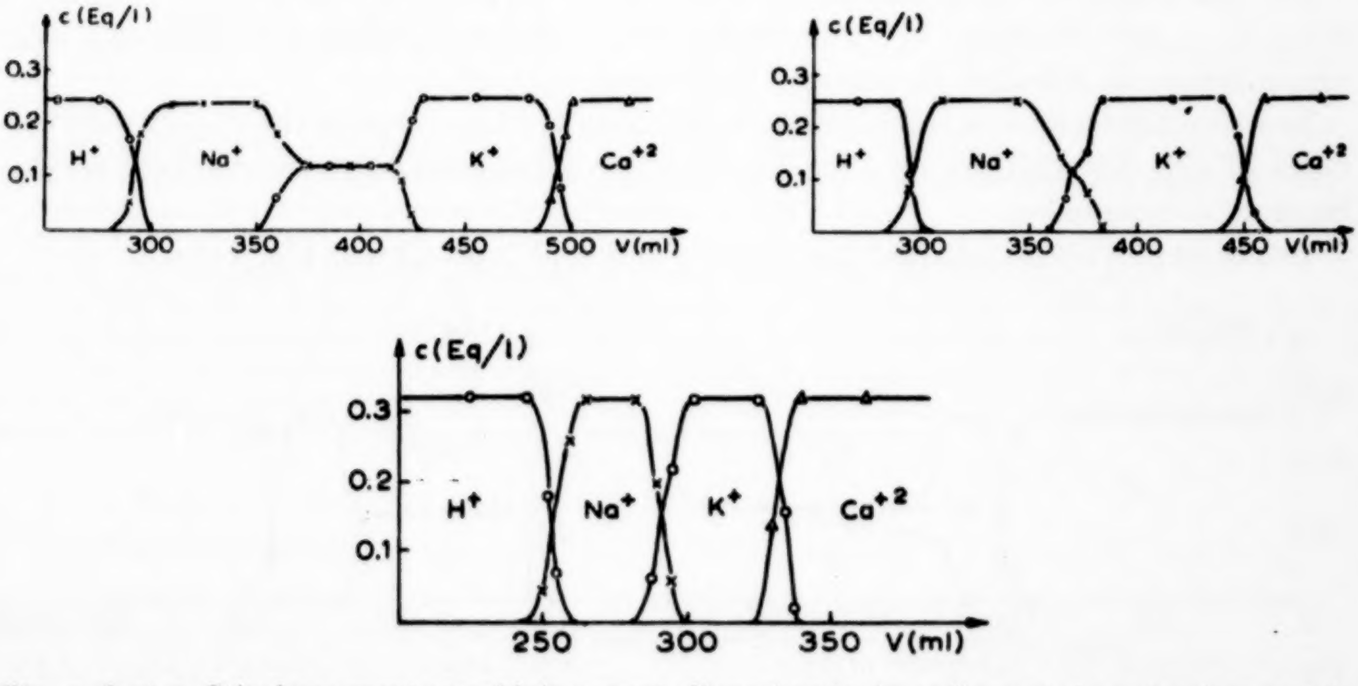

Fig. 7, 8 et 9. Développement par déplacement d'une bande de sodium et de potassium par le calcium.

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Sur la Fig. 7, on remarque que dans la bande mixte les ions Na$^+$ et K$^+$ sont dans les mêmes proportions qu'ils l'étaient initialement.

Deux essais analogues à celui représenté Fig. 9 ont été effectués mais dans un cas la bande initiale contenait 3 fois plus de sodium que de potassium et dans l'autre cas 3 fois plus de potassium que de sodium.

A la sortie de la colonne la séparation est effectuée comme dans les cas précédents.

RÉSUMÉ

Il est possible, dans le cas de la chromatographie d'échange d'ions, de prévoir les phénomènes se produisant lorsqu'on effectue une analyse frontale de deux ions, à partir de la connaissance des constantes d'équilibre.

Les résultats obtenus permettent de prévoir la séparation de deux corps effectuée selon la méthode du développement par déplacement. En particulier, on calcule la distance minimum à faire parcourir à une bande pour obtenir la séparation des solutés en zones.

La méthode est appliquée à la séparation des ions sodium et potassium au moyen de la résine Dowex-50 en utilisant l'ion calcium comme développeur.

SUMMARY

In the case of ion exchange chromatography it is possible to forecast, from the equilibrium constants, the phenomena that occur in frontal analysis of two ions.

With the results obtained the separation of two compounds by displacement development can be predicted. In particular it is possible to calculate the minimum distance that a band must travel to obtain a separation of the solutes in zones.

The method has been applied to the separation of sodium and potassium ions with the resin Dowex-50, using calcium ions as the developer.

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L'ANALYSE QUALITATIVE ET QUANTITATIVE DES HUILES LOURDES DE GOUDRON PAR CHROMATOGRAPHIE GAZEUSE

par

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INTRODUCTION

L'analyse détaillée conduisant à l'établissement de la composition centésimale des huiles lourdes de goudron, comme les huiles naphtaléniques (fraction bouillant de 200 à 230°C), les huiles de lavage (fraction 225-300°C) et les huiles anthracéniques (fraction 300-360°C), s'était révélée jusqu'ici impossible surtout dans le cadre d'un programme routinier de contrôle; tout au plus devait-on se contenter de tests assez simples comme la détermination d'une courbe de distillation standard et de quelques autres paramètres physiques (densité, point de congélation, viscosité, etc.) suivie du dosage chimique de quelques composants importants comme le naphtalène et l'anthracène.

BLOM ET EDELHAUSEN[1] ont récemment introduit l'analyse des constituants légers de l'huile de lavage, analyse basée sur une séparation préalable de ces substances dans une colonne chromatographique et dosage de l'anhydride carbonique formé lors de la combustion, dans un four à oxyde de cuivre, des corps élués de la colonne.

Nous inspirant des tendances actuelles vers la construction d'appareils de chromatographie en phase gazeuse fonctionnant à haute température, nous sommes parvenus à mettre au point une installation simple et peu coûteuse permettant l'analyse complète des huiles lourdes de goudron, celà avec une facilité telle que leur contrôle quantitatif ne pose plus de problèmes et peut entrer ainsi dans la pratique courante d'un laboratoire industriel.

La méthode de calcul des résultats qui est proposée ici rend l'analyse très rapide et indépendante, dans une large mesure, des paramètres de la colonne chromatographique, supprimant la nécessité d'une standardisation préalable des conditions opératoires.

PARTIE EXPÉRIMENTALE

Appareillage (voir Fig. 1)

Il est classique dans son principe mais ses dispositions particulières ont été choisies de façon à permettre aisément le travail à haute température.

La colonne est en tube de pyrex de 6-8 mm de diamètre, entièrement soudée après remplissage; cette technique évite les difficultés rencontrées, aux hautes températures, avec les raccords en verre rodé ou en caoutchouc de silicone.

Les catharomètres sont également réalisés en pyrex (voir Fig. 2) et soudés directement à la colonne; ils sont installés dans le four de façon à supprimer toute condensation de produits lourds.

D'un diamètre intérieur de 6 mm, ils sont équipés d'un fil de platine de 0.02 mm × 10 cm (R = 25 ohms), montés en pont de Wheatstone et chauffés sous 11 V^2. Un enrégistreur électronique inséré dans le pont trace directement la courbe chromatographique.

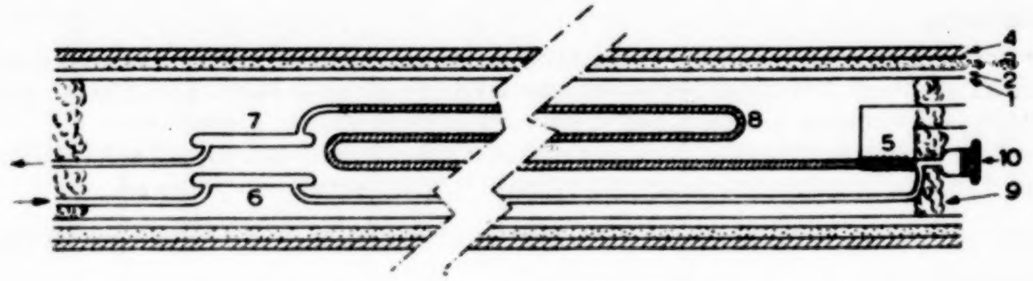

Fig. 1. Colonne chromatographique.

1. Blindage.
2. Tube pyrex.
3. Enroulement de chauffage.
4. Amiante.
5. Chauffage d'appoint.
6. Catharomètre d'entrée.
7. Catharomètre de sortie.
8. Colonne.
9. Ouate de verre.
10. Bouchon à sérum.

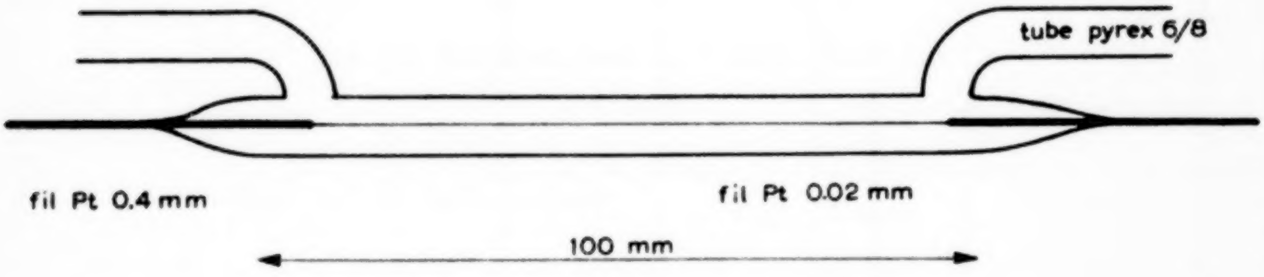

Fig. 2. Catharomètre en verre.

Les échantillons à analyser sont introduits à l'aide d'une microseringue à injection, à travers un bouchon à sérum[2]. Les produits solides sont préalablement dissous dans du benzène ou tout autre solvant convenable.

Il est très important d'assurer la volatilisation instantannée de l'échantillon: on y parvient à l'aide d'une résistance d'appoint de 60 watts bobinée en tête de colonne autour d'une zone remplie de ouate de verre dans laquelle pénètrera la pointe de l'aiguille d'injection; celle-ci sera de 10 cm de long de façon à pouvoir tenir le bouchon à sérum hors de la zone chaude de l'appareil.

L'ensemble colonne-catharomètres et accessoires est avantageusement fixé sur une plaque d'amiante qui permettra l'installation aisée du tout dans le four.

Le four, calorifugé avec du ruban d'amiante, est constitué par un tube de pyrex de 60 mm de diamètre et de 1.40 m de long sur lequel est bobinée régulièrement une résistance, de 1000 watts maximum, alimentée par un autotransformateur variable. Pour éviter tout effet d'induction sur les catharomètres, le bobinage sera non inductif et un blindage en tôle de cuivre sera prévu sur la paroi interne du four. Un long thermomètre, plongé dans l'enceinte, permettra d'en suivre la température.

Système chromatographique

Après divers essais, le système suivant a été adopté:

(a) La phase stationnaire est constituée par de la graisse de silicone (Dow Corning high vacuum Silicone Grease — U.S.A.) imprégnant de la brique réfractaire (Sil-O-Cell C 22 fire brick de Johns — Manville — U.S.A.)[3] broyée et tamisée au calibre de 60-80 mesh. Rapport silicone-brique = 30/100.

Il ne s'est pas montré nécessaire de purifier la graisse de silicone en notre possession suivant la technique de CROPPER ET HEYWOOD[4], mais il est possible que certains lots demandent une telle purification.

La longueur utile de la colonne est de 2.50 m, elle a été repliée en trombone pour en diminuer l'encombrement.

Une telle colonne peut fonctionner plusieurs mois de suite à 235°C sans perdre de son efficacité.

(b) L'hélium (Hélium Médical à 99.80% de l'Air Liquide — Belgique) a été choisi comme phase mobile dans le but d'avoir une plus grande sensibilité à la détection ainsi que des réponses égales pour tous les corps analysés. Un détendeur de précision à deux étages (Air Liquide) et un manomètre à mercure assurent un débit régulier et facilement réglable.

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Analyse qualitative

Avec une colonne de 2.50 m de long et un débit d'hélium de 50 cc/min (pression d'entrée 350 mm de Hg, sortie à l'air libre), l'analyse des huiles lourdes de goudron se montre rapide (30 à 60 minutes), la température étant choisie de 200 à 250°C suivant le type d'huile à analyser.

Une prise de 5 à 10 μl suffit pour l'analyse qualitative et quantitative; si l'échantillon est solide, on le dissout dans du benzène (environ 50/50) mais la prise sera alors de 20 μl.

Les Figs. 3a, 3b et 3c montrent des chromatogrammes de diverses huiles obtenus dans ces conditions.

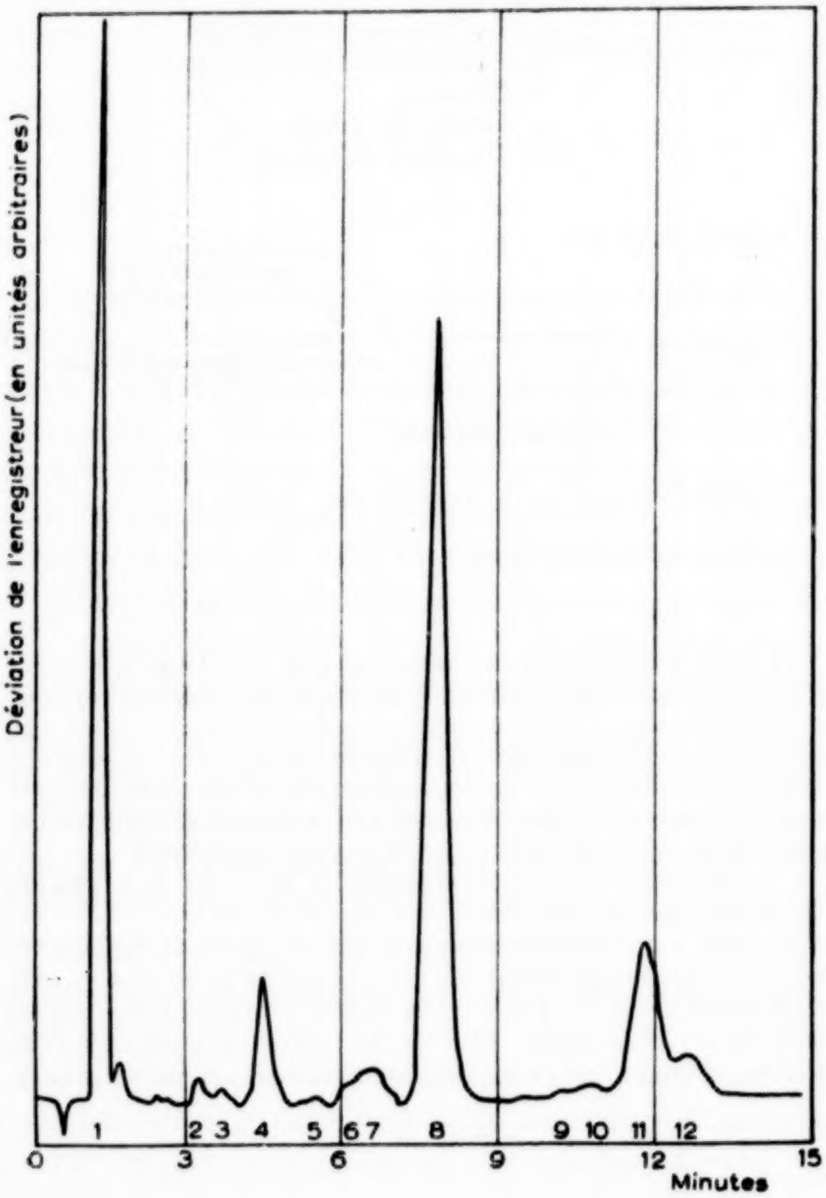

Fig. 3a. Chromatogramme d'huile naphtalénique.

1. Solvant.
2. Pseudo-cumène.
3. Hémellitène?
4. Indène.
5. Durène.
6. *o*- et *m*-Crésols?
7. Méthyl-indène?
8. Naphtalène.
9. Pseudo-cuménol?
10. Oxy-coumarone?
11. β-Méthyl naphtalène.
12. α-Méthyl naphtalène.

Le Tableau I regroupe les temps de rétention relatifs, T_R rel., (naphtalène = 1) des divers hydrocarbures rencontrés dans les huiles; ils ont été déterminés à partir de produits purs.

La relation linéaire qui existe entre les logarithmes des temps de rétention et les points d'ébullition (Fig. 4) doit être attribuée à la similitude des propriétés des hydrocarbures examinés. Cette relation peut être mise à profit pour identifier des produits dont on ne possède pas d'échantillon de référence.

Analyse quantitative

Le dosage des constituants rencontrés est très aisément réalisé par la méthode de normalisation interne décrite ci-dessous et qui avait été proposée par HAUSDORFF[6] pour

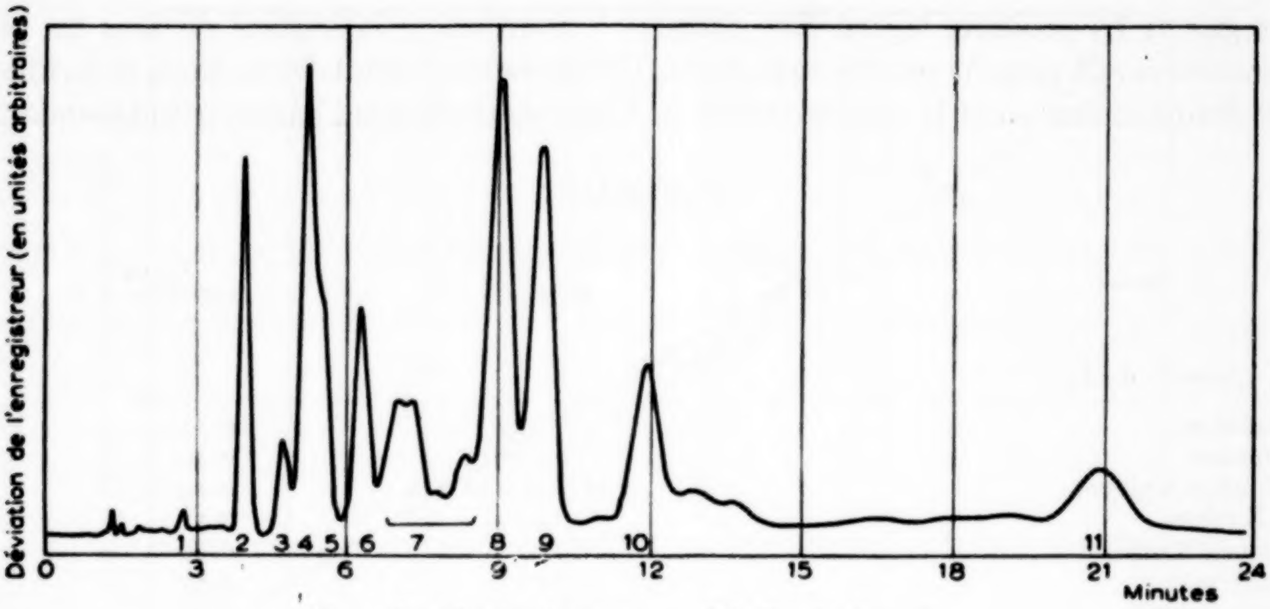

Fig. 3b. Chromatogramme d'huile de lavage.

1. Indène.
2. Naphtalène.
3. ?
4. β-Méthylnaphtalène.
5. α-Méthylnaphtalène.
6. Diphényle.
7. Diméthylnaphtalènes.
8. Acénaphtène.
9. Oxyde de diphénylène.
10. Fluorène.
11. Phénanthrène et anthracène.

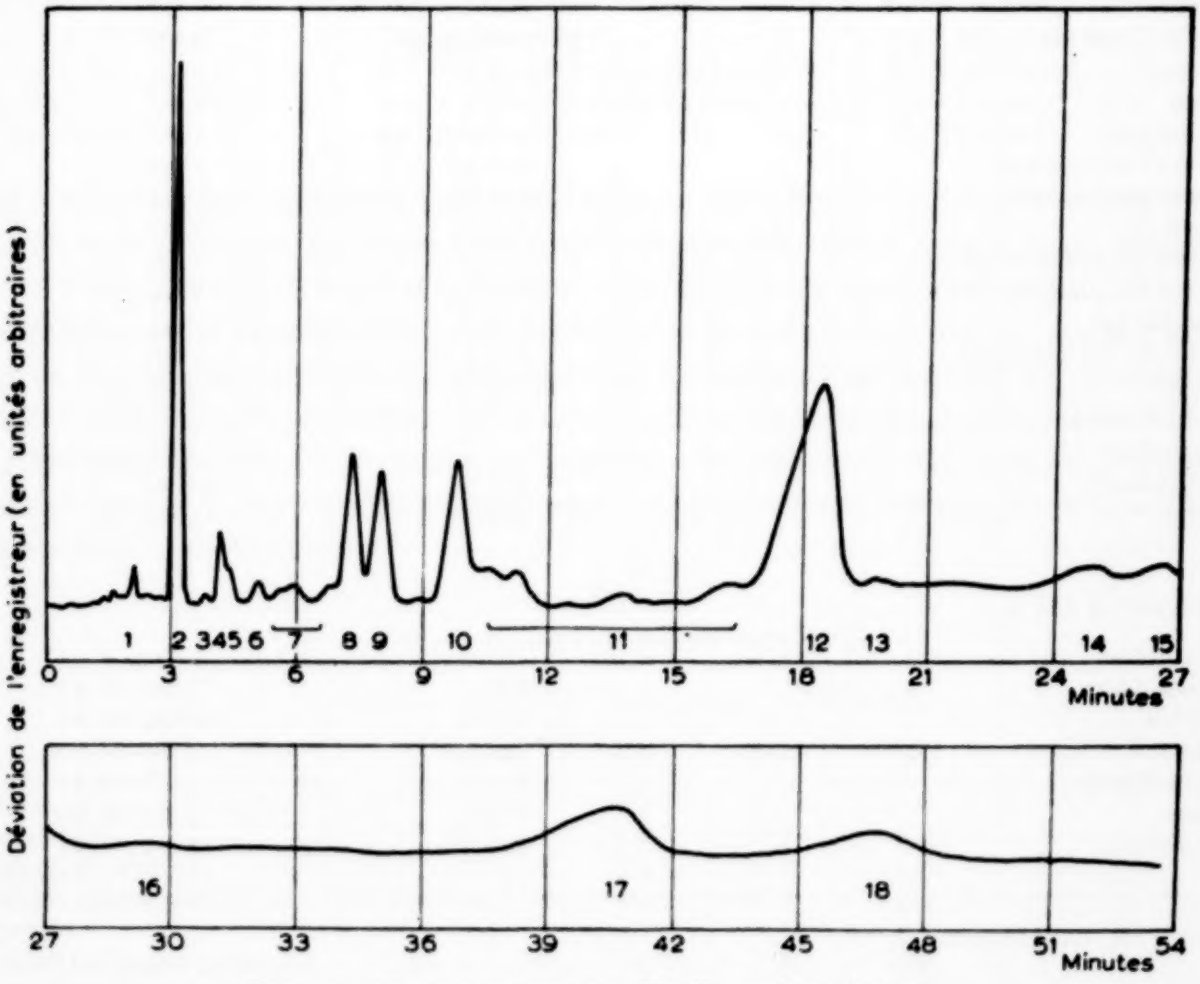

Fig. 3c. Chromatogramme d'huile anthracénique.

1. Indène.
2. Naphtalène.
3. ?
4. β-Méthylnaphtalène.
5. α-Méthylnaphtalène.
6. Diphényle.
7. Diméthylnaphtalènes.
8. Acénaphtène.
9. Oxyde de diphénylène.
10. Fluorène.
11. ?
12. Phénanthrène et anthracène.
13. Carbazol?
14. ?
15. Méthylanthracène?
16. Méthylcarbazol?
17. Fluoranthène.
18. Pyrène.

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les gaz et les produits légers. Elle consiste à additionner la surface de tous les pics rencontrés et à poser la somme égale à 100. Le rapport à ce total des surfaces individuelles donne directement la concentration %. Cette méthode rend l'analyse indépendante des paramètres choisis pour la colonne et permet même de doser les corps qui n'ont pas pu être identifiés.

TABLEAU I

Produit	*T d'ébul. °C*[5]	*T_R rel. (naphtalène = 1)*
a. Colonne à 185°C		
Benzène	80.2	0.15
Toluène	110.6	0.20
m- et *p*-Xylènes	138.3 et 139.0	0.29
o-Xylène	144.4	0.31
pseudo-Cumène	169	0.40
Indène	183.1	0.57
Naphtalène	217.9	1.00
β-Méthylnaphtalène	241.0	1.47
α-Méthylnaphtalène	244.6	1.57
b. Colonne à 235°C		
Benzène	80.2	0.20
Toluène	110.6	0.29
m- et *p*-Xylènes	138.3 et 139.0	0.40
o-Xylène	144.4	0.42
Indène	183.1	0.67
Naphtalène	217.9	1.00
β-Méthylnaphtalène	241.0	1.37
α-Méthylnaphtalène	244.6	1.44
Diphényle	254.9	1.67
2,6-Diméthylnaphtalène	262.0	1.86
1,2-Diméthylnaphtalène	271.4	2.22
Acénaphtène	276.9	2.44
Oxyde de diphénylène	285.1	2.66
Fluorène	297.9	3.25
Phénanthrène	336.8	5.81
Anthracène	340.7	5.81
Fluoranthène	383.5	12.90
Pyrène	393.5	15.00
c. Colonne à 295°C		
Naphtalène	217.9	1.00—0.33*
Acénaphtène	276.9	1.80—0.52
Fluorène	297.9	2.00—0.65
Anthracène	340.7	3.06—1.00
Fluoranthène	383.5	4.18—1.37
Pyrène	393.5	5.17—1.69
Chrysène	440.7	5.93—1.91

* T_R rel. (Anthracène = 1).

La surface des pics se détermine généralement par planimétrie oú, géométriquement, en multipliant la hauteur des pics par leur largeur à mi-hauteur. Cette dernière méthode, la plus couramment utilisée[7], présente cependant des défauts qui limitent son

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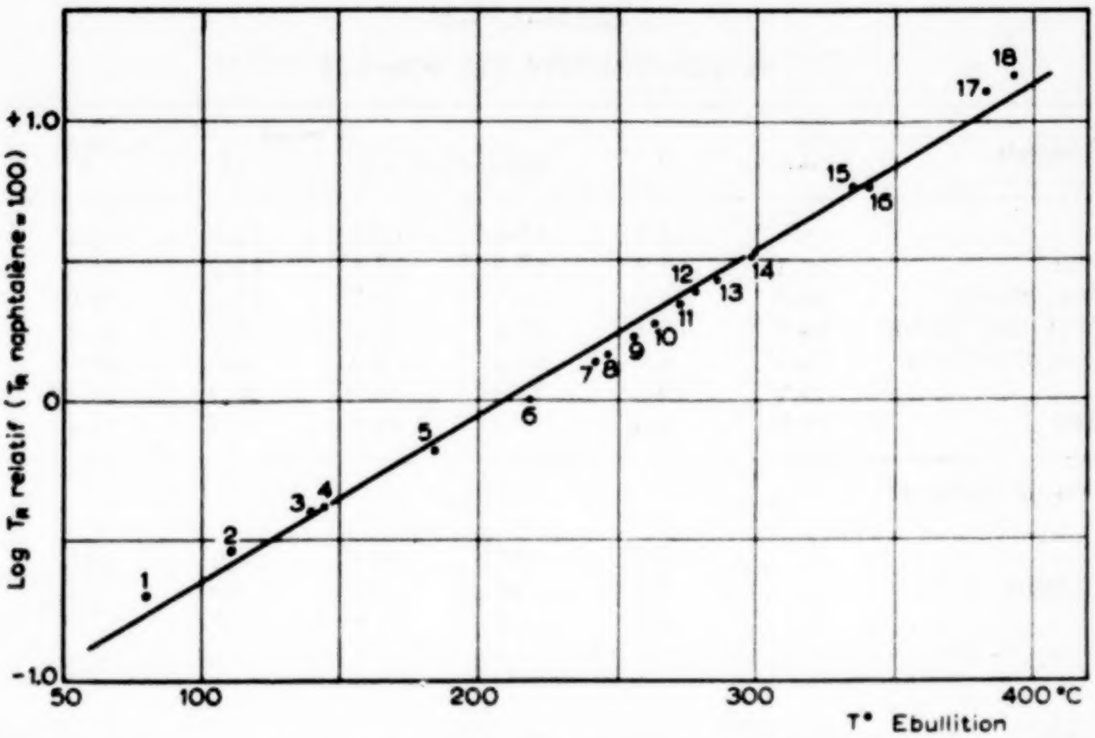

Fig. 4. Relation entre log T_R et la température d'ébullition des hydrocarbures aromatiques.

1. Benzène.
2. Toluène.
3. *m*- et *p*-Xylènes.
4. *o*-Xylène.
5. Indène.
6. Naphtalène.
7. *β*-Méthylnaphtalène.
8. *α*-Méthylnaphtalène.
9. Diphényle.
10. 2,6-Diméthylnaphtalène.
11. 1,2-Diméthylnaphtalène.
12. Acénaphtène.
13. Oxyde de diphénylène.
14. Fluorène.
15. Phénanthrène.
16. Anthracène.
17. Fluoranthène.
18. Pyrène.

usage; sa précision diminue très vite lorsque les pics sont étroits et elle n'est applicable que lorque les séparations sont complètes. Aussi avons-nous préféré la méthode consistant à multiplier la hauteur des pics par les temps de rétention[8].

La précision est satisfaisante, compte tenu de la complexité des mélanges étudiés. On peut cependant l'améliorer légèrement en multipliant les valeurs % trouvées par des facteurs de correction établis à partir de l'analyse de mélanges synthétiques connus.

Le Tableau II donne les résultats d'analyses effectuées sur des mélanges synthétiques, tandis que le Tableau III souligne que ces résultats sont largement indépendants des paramètres de la colonne.

TABLEAU II

ANALYSE DE MÉLANGES SYNTHÉTIQUES

Composés	*Mélange I*		*Mélange II*		*Mélange III*	
	% *calcule*	% *trouvé*	% *calculé*	% *trouvé*	% *calculé*	% *trouvé*
Indène	4.4	3.7	—	—		
Naphtalène	83.1	83.1	6.9	6.7		
β-Méthylnaphtalène	6.9	7.3	10.8	12.6		
α-Méthylnaphtalène	5.6	5.9	14.6	14.3		
Diphényle	—	—	5.3	5.4		
2,6-Diméthylnaphtalène	—	—	7.0	7.2		
1,2-Diméthylnaphtalène	—	—	4.0	3.5	31.6	29.4
Acénaphtène	—	—	19.0	18.3	—	—
Oxyde de diphénylène	—	—	15.8	16.3	—	—
Fluorène	—	—	8.4	9.2	8.9	9.4
Anthracène	—	—	8.2	6.5	18.5	20.2
Fluoranthène	—	—	—	—	17.6	18.4
Pyrène	—	—	—	—	23.4	22.6

TABLEAU III

REPRODUCTIBILITÉ DES MESURES

Composés	% *calc.*	% *trouvé*					
		I	*II*	*III*	*IV*	*V*	*VI*
Indène	15.9	15.6	16.1	15.7	14.8	14.1	12.4
Naphtalène	17.3	18.3	18.6	18.1	17.7	17.5	17.2
α-Méthylnaphtalène	20.0	20.3	20.1	19.8	19.3	19.6	19.9
1,2-Diméthylnaphtalène	15.8	16.4	16.2	16.3	16.2	17.2	16.8
Oxyde de diphénylène	9.5	9.8	10.1	9.4	9.8	10.0	10.5
Fluorène	9.9	10.3	10.1	10.1	10.4	10.2	11.1
Anthracène	11.6	9.3	8.8	10.6	11.8	11.4	12.1
Paramètres de colonne:							
Temp. °C		217°	216°	215°	239°	237°	241°
Hélium cc/min		42	42	30	30	54	54
Prise μl		10	8	8	8	8	15

Le Tableau IV regroupe les analyses effectuées sur trois types d'huiles d'origine technique; il montre que la méthode opératoire que nous avons développée est applicable à l'examen de tout mélange d'hydrocarbures aromatiques allant du benzène (80.2°C) au pyrène (393.5°).

Remarques

1. La méthode de mesure décrite permet de doser séparément les α- et β-méthylnaphtalènes, bien que leur séparation soit loin d'être complète.
2. Tenant compte de la complexité de la fraction des diméthylnaphtalènes, on se contente d'un dosage global obtenu en sommant les résultats calculés sur les divers pics qui apparaissent à hauteur des diméthylnaphtalènes.
3. On n'a pu, dans les conditions opératoires utilisées, séparer le phénanthrène (336.8°) de l'anthracène (340.7°). La somme de ces deux produits est donc dosée globalement.
4. Certains produits secondaires n'ont pas été identifiés mais il est tenu compte de leur titre dans les résultats.
5. Un lavage acide puis alcalin des huiles examinées a montré qu'elles ne renfermaient pas de quantités dosables de corps basiques ou acides.

CONCLUSIONS

L'analyse chromatographique en phase gazeuse se révèle de plus en plus un outil analytique de première importance pour l'étude des mélanges volatilisables. L'appareillage nécessaire peut être facilement réalisé et mis en oeuvre dans un laboratoire industriel.

Le mode opératoire décrit dans le présent travail rend désormais possible l'analyse détaillée des huiles lourdes de goudron, notamment des huiles de lavage et anthracénique.

Cette analyse précise et aisée est susceptible de rendre de grands services pour le contrôle et le réglage fin de la distillation du goudron, comme pour la mise en oeuvre des produits issus de cette distillation ou la préparation de coupages spéciaux.

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TABLEAU IV

EXEMPLES D'ANALYSE D'HUILES DE GOUDRON

Composés	*Huiles*		
	naphtalénique	*lavage*	*anthracénique*
Benzène	—	0.2%	—
?	—	0.1	—
Toluène	—	0.4	—
Xylènes	—	0.1	—
?	—	0.1	—
pseudo-Cumène	0.3%	0.2	—
Indène	2.0	0.7	0.3%
?	0.5	—	—
?	0.5	—	—
Naphtalène	86.2	6.5	6.1
?	0.3	—	—
β-Méthylnaphtalène	7.6	22.0	1.5
α-Méthylnaphtalène	2.6	11.0	0.6
Diphényle	—	7.1	0.6
Diméthylnaphtalènes	—	9.9	1.4
?	—	1.7	—
Acénaphtène	—	21.4	4.3
Oxyde de diphénylène	—	11.0	5.5
?	—	1.3	—
Fluorène	—	4.9	10.3
?	—	1.4	2.4
?	—	—	2.3
?	—	—	1.6
?	—	—	2.5
Anthracène Phénanthrène	—	—	26.4
Carbazol?	—	—	6.0
?	—	—	3.7
Méthylanthracène?	—	—	5.0
Méthylcarbazol?	—	—	2.2
Fluoranthène	—	—	10.7
Pyrène	—	—	6.6

La méthode proposée pourra évidemment être appliquée à d'autres huiles lourdes, des huiles de pétroles, etc.

REMERCIEMENTS

Les auteurs désirent remercier la Gesellschaft für Teerverwertung à Duisburg qui a bien voulu mettre gracieusement à leur disposition les hydrocarbures purs qui ont servi de référence.

Leurs remerciements vont également à Monsieur P. FERRERO, Directeur Général des Recherches, pour l'appui éclairé trouvé auprès de lui au cours de leurs travaux.

RÉSUMÉ

On décrit une méthode de chromatographie gazeuse permettant l'analyse qualitative et quantitative rapide des huiles lourdes de goudron: naphtalénique, de lavage, anthracénique, etc.

L'appareil peut être facilement réalisé dans un laboratoire industriel. Quant aux résultats, ils sont calculés par une méthode très simple de normalisation interne ne demandant pas d'étalonnage préalable.

On donne la composition de quelques huiles, déterminée par la méthode proposée.

SUMMARY

A method of gas chromatography is described for the rapid qualitative and quantitative analysis of tar heavy oils: naphthalenic oils, wash oils, anthracenic oils, etc.

The apparatus used can be easily constructed in an industrial laboratory. The results are calculated by a very simple method of internal normalization requiring no previous standardization.

The composition of various oils, determined by the proposed method, is given.

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Reçu le 22 juillet 1957

ELEKTROPHORESE DER HALOGENOKOMPLEXE VON Hg(II), Bi(III), Cd(II), Pb(II) UND Cu(II)

III. CHLORO-, BROMO- UND JODOKOMPLEXE IN KCl, HCl, KBr, HBr UND KJ

von

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EINLEITUNG

Die elektrophoretischen Beweglichkeiten der Chlorokomplexe der Metalle Hg, Bi, Cd, Pb und Cu in Chlorwasserstoffsäure wurden in früheren Mitteilungen[1,2] erörtert. Unter Beibehaltung gewisser experimentellen Massnahmen wurde es mittels Starkstromelektrophorese ermöglicht, die Diagramme der elektrophoretischen Beweglichkeiten der Chlorokomplexe als Funktion der Chlorwasserstoffsäurekonzentration zu erhalten[1].

In vorliegender Mitteilung wollen wir die Beweglichkeiten anderer Halogenokomplexe der genannten Metalle experimentell verfolgen. Im Laufe der Experimente wurde es ersichtlich, dass die Beweglichkeiten der Metallokomplexe, wie übrigens auch zu erwarten war, annähernd eine exponentielle Funktion der Konzentration der komplexierenden Reagentien zu sein scheinen (vergl. Mittlg. I[1] Fig. 3). Deswegen haben wir uns entschlossen, in dieser Mitteilung die Diagramme der Beweglichkeiten in dem Sinne zu ändern, dass wir die Konzentrationen des komplexierenden Reagens an der Abszisse nicht linear, sondern logarithmisch wiedergeben. Auf diese Weise erhalten wir Geraden mit charakteristischen Neigungen und Knickpunkten.

EXPERIMENTELLER TEIL

1. Die Diagramme der elektrophoretischen Beweglichkeiten

Für methodische und experimentelle Einzelheiten vergleiche Mitteilung I[1].

Die Fig. 1, 2 und 3 geben die Beweglichkeiten der Halogenokomplexe von Hg(II), Bi(III), Cd(II), Pb(II) und Cu(II) wieder. Oberhalb der Abszissenachse wandern alle Ionen anionisch, und unterhalb der Abszissenachse kationisch.

Sämtliche elektrophoretische Beweglichkeiten wurden gemäss Gleichung 5, Mittlg. I, korrigiert.

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In Fig. 1 wurden die Beweglichkeiten der Chlorokomplexe in HCl, um sie mit denen in KCl vergleichen zu können, aus Mittlg. I, Fig. 3 entnommen, und in das Koordinatensystem mit logarithmisch geteilter Abszisse aufgetragen.

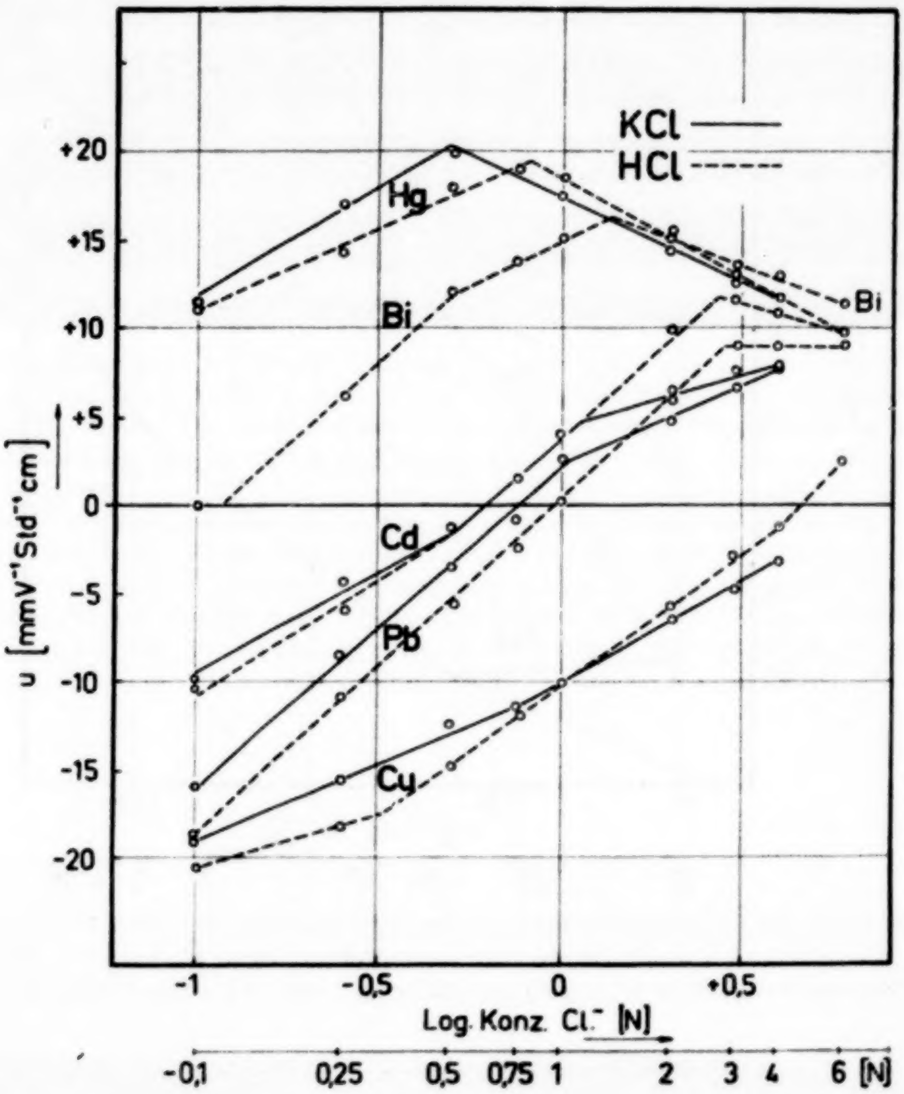


Fig. 1. Die Diagramme der elektrophoretischen Beweglichkeiten der Chlorokomplexe in KCl und HCl von Hg, Bi, Cd, Pb und Cu. Ordinate: die korrigierten Beweglichkeiten in (mm. Volt^{-1}. Std.$^{-1}$. cm). Abszisse: Logarithmus der Konzentration von KCl (0.1 bis 4*N*) und HCl (0.1 bis 6*N*). Oberhalb der Abszissenachse wandern alle Ionen anionisch, und unterhalb der Abszissenachse kationisch. Filtrierpapier Munktel No. 20/150, Temperatur 20 - 21°C.

2. *Elektrophoretische Trennungen eines Gemisches von Hg-Bi-Cd-Pb-Cu in KCl, KBr und HBr*

Fig. 4 gibt die Trennung in 0.1*N* KCl (1), 0.5*N* KCl (2), 1*N* KCl (3), 4*N* KCl (4), 0.5*N* KBr (5) und 1*N* KBr (6), und Fig. 5 in 0.1*N* HBr (1), 0.25*N* HBr (2), 0.5*N* HBr (3), 0.75*N* HBr (4) und 1*N* HBr (5) wieder.

Der Startstrich ist in der Mitte der Streifen, links war die Anode und rechts die Kathode. Alle Zonen sind vollkommen getrennt. Die Dimension der abgebildeten Streifen beträgt 660 mm × 15 mm. Die Dauer der Elektrophorese wurde bei diesen Experimenten so gewählt, dass die Länge der Papierstreifen möglichst gut ausgenützt, und vollkommene Trennung erzielt wurde. Für weitere Experimentaldaten vergleiche der Erläuterungen zu Fig. 4 und 5.

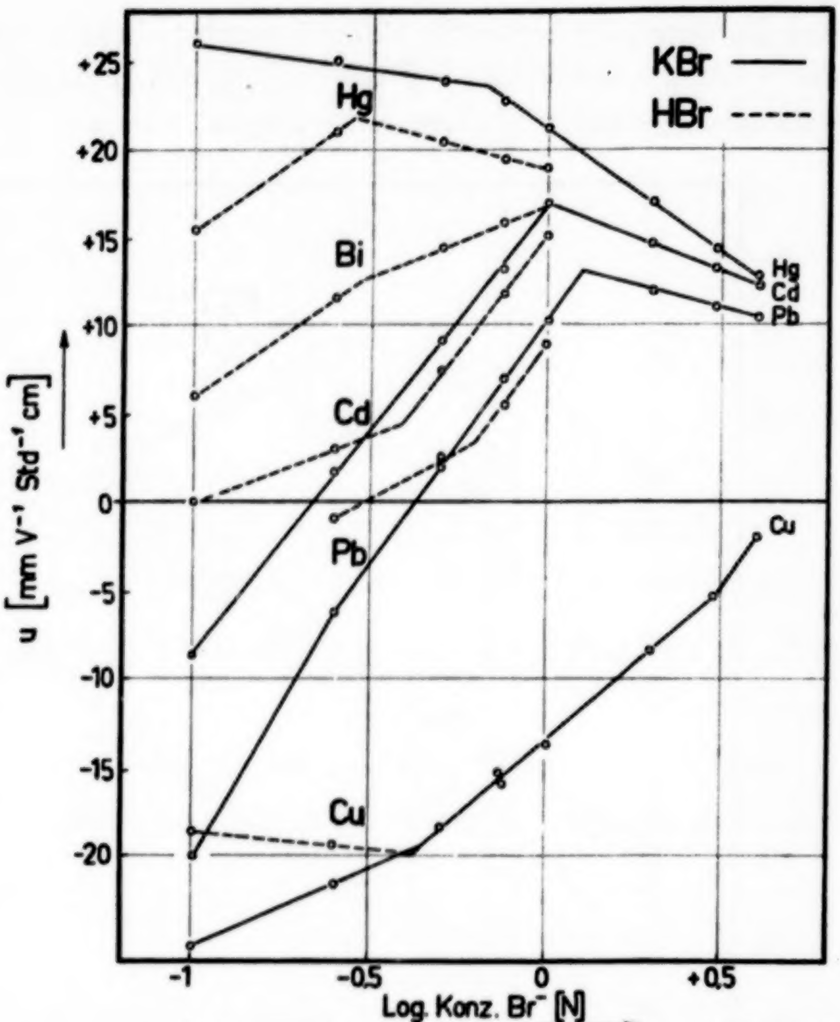


Fig. 2. Die Diagramme der elektrophoretischen Beweglichkeiten der Bromokomplexe in KBr und HBr von Hg, Bi, Cd, Pb und Cu. Ordinate: die korrigierten Beweglichkeiten. Abszisse: Logarithmus der Konzentration von KBr (0.1 bis 4*N*) und HBr (0.1 bis 1*N*). Alles Übrige wie Fig. 1.

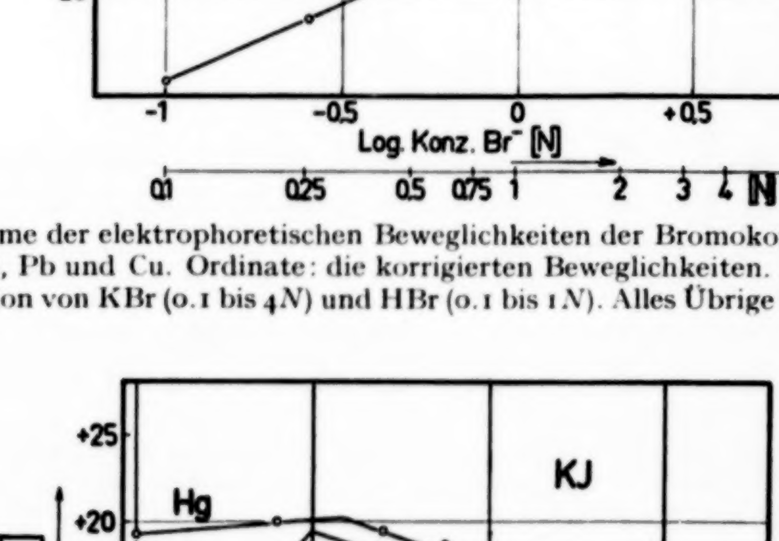
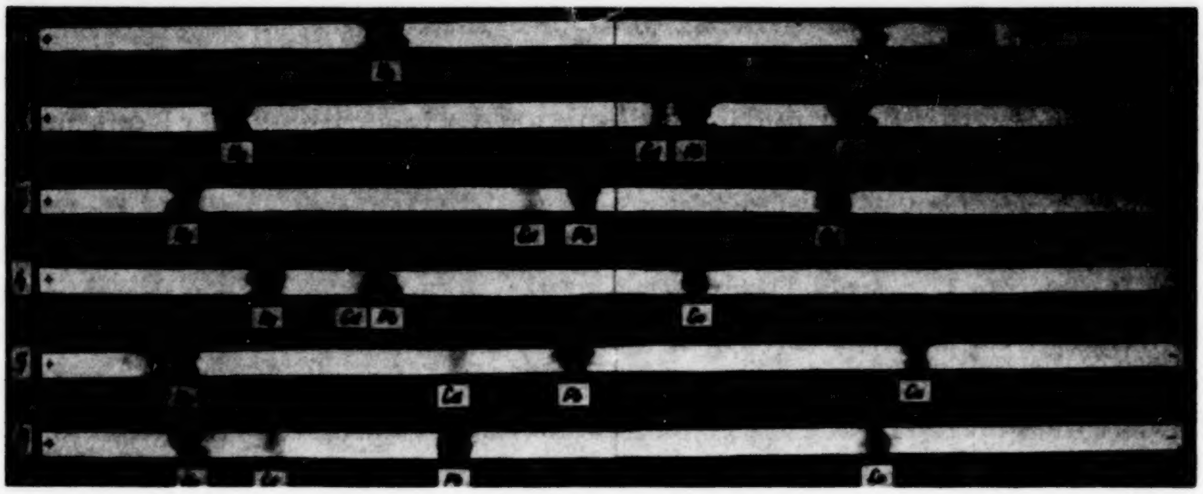


Fig. 3. Die Diagramme der elektrophoretischen Beweglichkeiten der Jodokomplexe in KJ (0.1 bis 4*N*) von Hg, Cd, Pb und Cu. Alle Komplexe sind anionisch. Die schwerlöslichen Jodide des Cu und Pb werden erst in *ca.* 1.5*N*, bzw. 2*N* KJ gelöst. Von 0.1*N* KJ bis 0.5*N*, bzw. 0.75*N* KJ bleiben die Zonen der unlöslichen Jodide des Cu und Pb am Startpunkt liegen. Im Gebiet der gestrichelten Geraden sind die Zonen des Cu und Pb, wegen teilweiser Unlöslichkeit der Jodide, unscharf. Alles Übrige wie Fig. 1.



* Fig. 4. Die Elektropherogramme der Trennung Hg – Cd – Pb – Cu in 0.1N KCl (1), 0.5N KCl (2). 1N KCl (3), 4N KCl (4), 0.5N KBr (5) und 1N KBr (6). Der Startstrich ist in der Mitte, links die Anode, rechts die Kathode. Die Dimensionen der abgebildeten Papierstreifen sind 660 mm × 15 mm. Die beste Trennung wurde in 0.5N KBr erzielt.

Die Elektrophoresedaten:

1. 0.1N KCl, $H = 36.4$ V/cm, $I = 30$ mA/1.5 cm, $\triangle E = 2400$ V, $N = 72$ Watt, $t = 21$°C, $\tau = 0.5$ Std.
2. 0.5N KCl, $H = 20.4$ V/cm, $I = 56$ mA/1.5 cm, $\triangle E = 1350$ V, $N = 75$ Watt, $t = 21$°C, $\tau = 0.7$ Std.
3. 1N KCl, $H = 15.15$ V/cm, $I = 72$ mA/1.5 cm, $\triangle E = 1000$ V, $N = 72$ Watt, $t = 20$°C, $\tau = 1$ Std.
4. 4N KCl, $H = 7.88$ V/cm, $I = 137$ mA/1.5 cm, $\triangle E = 520$ V, $N = 71$ Watt, $t = 21$°C, $\tau = 2.75$ Std.
5. 0.5N KBr, $H = 20.4$ V/cm, $I = 56$ mA/1.5 cm, $\triangle E = 1350$ V, $N = 76$ Watt, $t = 21$°C, $\tau = 0.7$ Std.
6. 1N KBr, $H = 15.15$ V/cm, $I = 72$ mA/1.5 cm, $\triangle E = 1000$ V, $N = 72$ Watt, $t = 20$°C, $\tau = 1$ Std.

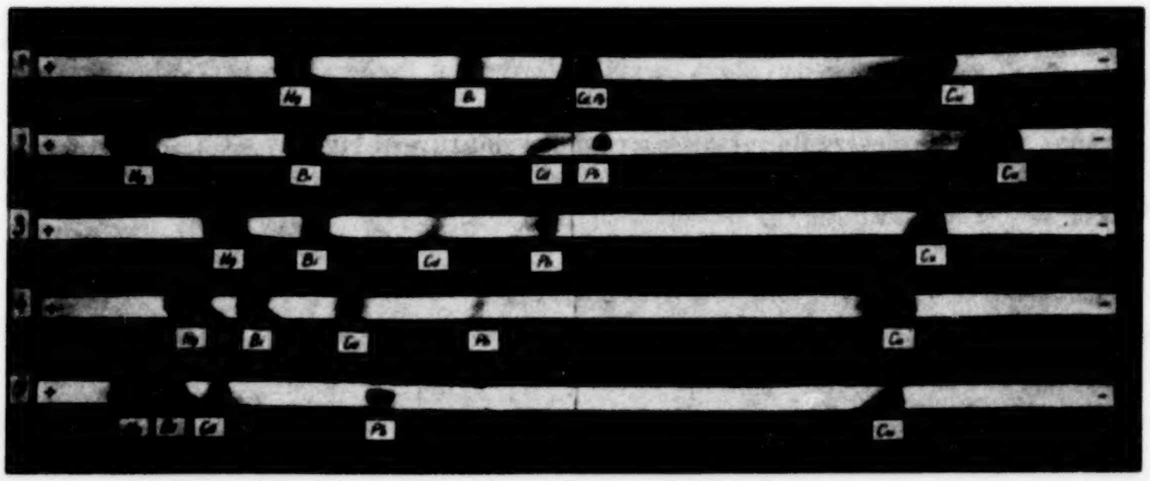


Fig. 5. Die Elektropherogramme der Trennung Hg – Bi – Cd – Pb – Cu in 0.1N HBr (1), 0.25N HBr (2), 0.5N HBr (3), 0.75N HBr (4) und 1N HBr (5). Die beste Trennung wurde in 0.5N HBr erzielt. Die Elektrophoresedaten:

1. 0.1N HBr, $H = 28$ V/cm, $I = 39$ mA/1.5 cm, $\triangle E = 1850$ V, $N = 72$ Watt, $t = 21$°C, $\tau = 0.53$ Std.
2. 0.25N HBr, $H = 16.1$ V/cm, $I = 66$ mA/1.5 cm, $\triangle E = 1060$ V, $N = 70$ Watt, $t = 21$°C, $\tau = 1$ Std.
3. 0.5N HBr, $H = 12.86$ V/cm, $I = 85$ mA/1.5 cm, $\triangle E = 850$ V, $N = 72$ Watt, $t = 21$°C, $\tau = 1$ Std.
4. 0.75N HBr, $H = 10.8$ V/cm, $I = 100$ mA/1.5 cm, $\triangle E = 720$ V, $N = 72$ Watt, $t = 21$°C, $\tau = 2.1$ Std.
5. 1N HBr, $H = 8.65$ V/cm, $I = 126$ mA/1.5 cm, $\triangle E = 570$ V, $N = 72$ Watt, $t = 21$°C, $\tau = 2.1$ Std.

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* Fotos: Aus dem Fotolaboratorium des Instituts Ruder Bošković.

SCHLUSSFOLGERUNG UND DISKUSSION

Wenn die elektrophoretischen Beweglichkeiten der Chloro-, Bromo- und Jodokomplexe von Hg, Bi, Cd, Pb, und Cu als Funktion des Logarithmus der Konzentration des entsprechenden Halogenions dargestellt werden, resultieren Geraden mit charakteristischen Neigungen, Knickpunkten und Parallelitäten. Aus solchen Diagrammen ist ersichtlich, dass die Neigung zur Komplexbildung einerseits in der Reihenfolge Chloro – Bromo – Jodo, und andererseits, im Falle von Chloro- und Bromokomplexen, in der Reihenfolge Cu – Pb – Cd – Bi – Hg anwächst. Bei Jodokomplexen ist die Reihenfolge (Pb+Cd) – Hg – Cu. Aus den Diagrammen und den Abbildungen der Trennungen ist es ersichtlich, dass die Trennung der genannten Metalle in Form von Halogenkomplexen am besten in 0.5*N* KBr, bzw. 0.5*N* HBr gelingt.

ZUSAMMENFASSUNG

Die durch Starkstromelektrophorese am Filterpapier erzeugten elektrophoretischen Beweglichkeiten der Chloro-, Bromo- und Jodokomplexe von Hg, Bi, Cd, Pb und Cu wurden als Funktion des Logarithmus der Konzentrationen der Halogenionen graphisch dargestellt. Als komplexierende Reagentien wurden KCl, HCl, KBr, HBr und KJ gewählt, und zwar hauptsächlich in Konzentrationen von 0.1*N* bis 4*N*. Daraus resultierten Geraden mit charakteristischen Neigungen, Knickpunkten und Parallelitäten. Weiter ist aus den Diagrammen ersichtlich, dass die Neigung zur Komplexbildung einerseits in der Reihenfolge Chloro – Bromo – Jodo, und andererseits, bei Chloro- und Bromokomplexen, in der Reihenfolge Cu – Pb – Cd – Bi – Hg anwächst. Bei Jodokomplexen ist die Reihenfolge (Pb + Cd) – Hg – Cu.

Elektrophoretische Trennungen eines Gemisches von Hg – Bi – Cd – Pb – Cu in verscheidenen Konzentrationen von KCl, KBr und HBr wurden illustriert. Die Trennung der genannten Metalle in Form von Halogenokomplexen gelingt bestens in 0.5*N* KBr, bzw. 0.5*N* HBr.

SUMMARY

The electrophoretic mobilities of chloro-, bromo- and iodo-complexes of Hg, Bi, Cd, Pb, and Cu, obtained by heavy current electrophoresis on filter paper, are presented in diagrams as a function of the logarithm of the concentrations of the halogen ions. KCl, HCl, KBr, HBr and KJ, mainly in concentrations between 0.1*N* and 4*N*, were selected as complexing agents. Straight lines were obtained with characteristic slopes, breaks and parallelisms. Furthermore it can be seen from the diagrams, that the tendency to form complexes increases on the one hand in the sequence chloro – bromo – iodo, and on the other for the chloro- and bromo-complexes in the sequence Cu – Pb – Cd – Bi – Hg. In the case of the iodo-complexes the sequence is (Pb + Cd) – Hg – Cu.

Figures that show the electrophoretic separtion of a mixture of Hg – Bi – Cd – Pb – Cu in various concentrations of KCl, KBr and HBr, are given. The separation of these metals in the form of halogeno-complexes can be most satisfactorily accomplished in 0.5*N* KBr or 0.5*N* HBr.

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Eingegangen den 29. Juli 1957

APPLICATION OF THE ROTATED DROPPING MERCURY ELECTRODE TO THE ANALYSIS OF MIXTURES OF ELECTROACTIVE SUBSTANCES*

by

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The rotated dropping mercury electrode (RDME) recently developed in this laboratory[1] has potentialities in trace determinations by virtue of its high sensitivity. It allows polarographic determinations at concentrations of the order of ten times smaller than with the conventional dropping mercury electrode (DME). The limiting current at the RDME is proportional to the concentration of electroactive species to be electrolyzed, as has previously been shown experimentally by STRICKS AND KOLTHOFF[1] and theoretically by OKINAKA AND KOLTHOFF[2]. In the application of the RDME for analytical purposes it must be realized that it is almost imperative to determine limiting currents in the presence of a suitable capillary active substance and that the quantitative dependence of the limiting current upon various factors is entirely different from that of the diffusion current at the DME on these factors. The variation of limiting current with drop time is especially important when interpreting polarograms of mixtures of electroactive constituents for analytical purposes, and this is the main subject of this paper.

In the absence of surface active substances the current at the RDME involves so-called maxima of the second kind, which arise from streaming at the mercury-solution interface and are characterized by the occurrence of a maximum in current-potential curves at the electrocapillary zero potential. The current involving such maxima is very sensitive to even trace amounts of surface active substances which are usually present in the solution as impurity. Accordingly, in order to obtain reproducible results in current measurements, the maxima must be suppressed completely by adding a sufficient amount of a suitable surface active substance. For general analytical purposes it is desirable that the surface active compound be kept adsorbed on the mercury surface between the dissolution potential of mercury and the decomposition potential of the supporting electrolyte. There must be no chemical interaction between the capillary active substance and the species to be analyzed. Gelatin suppresses maxima at the RDME over the entire potential range. However, particularly at the negative side of its isoelectric point it tends to combine with several metal ions and thus causes a decrease of the ratio of limiting current to concentration (Table I). This effect is rarely noticed at the DME because, as a rule, the ratio of concentration of gelatin to that of

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** On leave from the University of Kyoto, Japan.

metal ion is such that the effect is negligible. At the RDME where concentrations can be some ten times or more smaller than at the DME the effect can become pronounced. Under such conditions the ratio of limiting current to concentration is not constant but increases with increasing concentration. Typical examples are given in a subsequent section. A systematic study of many capillary active substances has been made in order to find a suitable maximum suppressor[3]. Polyacrylamide appeared to be an ideal suppressor and is recommended for polarographic work both at the DME and at the RDME. It remains adsorbed over the entire potential range which can be covered at mercury and it does not combine with metal ions or other constituents tested so far.

When the maxima are thus completely suppressed, current-potential curves at the RDME become comparable in shape to those at the DME. However, the limiting current is dependent upon various factors in an entirely different manner than the diffusion current is at the DME. An extensive theoretical and experimental study of the limiting current in the presence of a suppressor at the RDME led to the following equation[3]:

$$i_1 = 230nCD^{1/2}\{m^{2/3}t^{1/6} + 103D^{1/2}(mt)^{1/6} + 5.76U^{1/2}\nu^{-1/6}D^{1/6}(mt)^{1/3}\}. \quad . \quad . \quad . \quad (1)$$

in which i_1 is the average limiting current at 25°C in μA, n the number of electrons involved in the electrochemical reaction, C the bulk concentration of the electroactive species in mM, D the diffusion coefficient in cm²/sec, m the rate of flow of mercury in mg/sec, t the drop time in sec, U the linear speed of rotation of the electrode in cm/sec and ν the kinematic viscosity of the solution in cm²/sec. If the first and second terms in the brackets of the above equation are neglected for the reason that the sum of these two terms is only 15% or less of the third term at suitable speeds of rotation ($\sim$ 200 r.p.m.), it follows as a first approximation that

$$i_1 \propto nCD^{2/3}U^{1/2}\nu^{-1/6}(mt)^{1/2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

As has been discussed in a previous paper[3], equation (1) or (2) holds only for electrodes with a relatively small orifice (< 0.7 mm in diameter) and a small distance between the orifice and center of rotation (< 8 mm). From the analytical viewpoint, electrodes with larger orifice (0.9–1 mm) are more favorable for trace analysis because of higher sensitivity of such electrodes. It was found[3] that at these more sensitive electrodes the limiting current is closely proportional to t raised to a power greater than 1/2, sometines close to one:

$$i_1 \cong kt^a \ (a > 1/2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

On the other hand, the diffusion current at the DME is given by the Ilkovic equation as a close approximation:

$$i_d = 607nCD^{1/2}m^{2/3}t^{1/6} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

From a comparison of expressions (2) or (3) with (4) it is evident that with a given capillary the limiting current at the RDME is more greatly affected by the drop time and hence by the potential than the diffusion current at the DME (see Fig. 5). This effect is of no consequence when the solution contains a single reducible component or when the component producing the first wave is the only substance to be determined, for in such cases the limiting current is always measured at the same potential. In the analysis of a mixture of two or more reducible substances this effect becomes important.

EXPERIMENTAL

Materials

Conductivity water and C. P. chemicals were used. Solutions of known concentration of thallium and iodate were prepared by dissolving weighed amounts of thallous chloride or potassium iodate in the appropriate amount of water. A manganese(II) solution was prepared by dissolving an approximately weighed amount of manganese sulfate in water. The manganese content was determined by oxidizing an appropriate amount of the solution with sodium bismuthate, adding an excess ferrous sulfate and titrating back with standard potassium permanganate solution. A solution of mercury(II) was prepared by dissolving mercuric nitrate in dilute nitric acid. This solution was standardized against potassium thiocyanate. A bismuth solution was prepared by dissolving a weighed amount of metallic bismuth in nitric acid and adjusting the volume. A solution of known concentration of copper(II) was obtained by dissolving an approximately weighed amount of cupric sulfate in water and determining the copper content iodometrically.

Stock solutions of gelatin of ordinary kind (Coignet "high grade") and gelatin of high isoelectric point* were prepared by dissolving 0.5 g of each in hot water, adding a few drops of toluene as preservative and diluting to 100 ml. A 0.5% stock solution of polyacrylamide (PAM 75, American Cyanamid Co., New York)* was prepared by dissolving the polymer in warm water. This solution is stable.

Current measurements

Currents were measured with a Leeds and Northrup Electrochemograph Type E, Sargent Polarograph Model XXI or a manual apparatus described by LINGANE AND KOLTHOFF[4]. The current measured with the pen-recording instruments by taking the middle point of current oscillations was checked frequently with the value measured with the manual apparatus, and the position of the damping switch of the automatic instruments was carefully selected so that values obtained with both types of instruments did not differ more than 2%. Our experience shows that, even when current oscillations appear to be properly damped, the average current measured with the recording instruments is different from the value obtained with the manual apparatus sometimes as much as 5%. Therefore, for accurate determinations it is recommended to use a manual apparatus. All experiments were carried out at 25.0 ± 0.1°C.

Electrodes

Two electrodes provided with an attachment to vary the height of the mercury column as described in a previous paper[3] were used. They had the following characteristics:

Electrode No.	a) *d* *mm*	b) Ø *mm*	*r.p.m.*	c) *h* *cm*	*t(open circuit) in 0.1 M KCl sec*	*m* *mg/sec*	d) α
1	5.16	0.5	210	96	4.54	7.79	0.56
2	6.55	0.9	210	58	4.18	11.19	0.84

[a] Distance between the orifice and center of rotation.

[b] Diameter of orifice.

[c] Height of mercury.

[d] *cf.* Figs. 6 and 7. Electrode 2 is about 40% more sensitive than electrode 1, but it does not follow the theoretical equation (1).

The tip of the end tube was treated with a liquid silicone preparation according to the directions given by STRICKS AND KOLTHOFF[1]. The effect of the height of mercury on the limiting current is so small that for analytical purposes the simpler RDME of the original design[1] without any attachment to vary the mercury pressure may be used as well.

The electrolysis vessel used was a beaker of 250 ml capacity, which was provided with a rubber stopper with holes for the electrode, for inlet and outlet tubes for nitrogen and for a tube with sintered glass bottom which holds the salt bridge. The volume of the solution was 100 ml in all experiments. Dissolved oxygen was removed by passing 99.99% pure Linde nitrogen for at least 30 min.

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* The courtesy of Dr. H. C. YUTZY of Eastman Kodak Research Laboratories in supplying a large number of samples of polymeric substances is gratefully acknowledged.

RESULTS AND DISCUSSION

Maximum suppressors

A generally applicable surface active substance used with the RDME as maximum suppressor must remain adsorbed at the mercury surface over the entire range of potentials. An extensive investigation performed in this laboratory with a large number of surface active compounds revealed that the majority of these compounds are desorbed from the mercury surface at potentials more positive than about —1.6 V *vs.* S.C.E. This is evidenced by the appearance of desorption waves on current–potential curves. A detailed description of these desorption waves will be given in a subsequent paper.

TABLE I

PROPORTIONALITY BETWEEN THE LIMITING CURRENT AND THE CONCENTRATION OF COPPER IN AMMONIACAL MEDIUM IN THE PRESENCE OF GELATINS AND POLYACRYLAMIDE

(Electrode No. 2, —0.7 V *vs.* S.C.E., 0.1*M* ammonia and 0.1*M* ammonium nitrate, currents corrected for the residual).

Concentration of copper mM	*Ordinary gelatin*				*High isoelec. pt. gelatin*				*Polyacrylamide*			
	0.01%		*0.04%*		*0.01%*		*0.02%*		*0.01%*		*0.02%*	
	$i_1(\mu A)$	i_1/C	$i_1(\mu A)$	i_1/C	$i_1(\mu A)$	i_1/C	$i_1(\mu A)$	i_1/C	$i_1(\mu A)$	i_1/C	$i_1(\mu A)$	i_1/C
0.00400	0.26	65	0.18	45	0.33	83	0.32	80	0.34	85	0.33	84
0.00800	0.60	75	0.40	50	0.66	83	0.65	81	0.68	85	0.67	84
0.0160	1.20	75	0.91	56	1.31	82	1.27	79	1.36	85	1.34	84
0.0320	2.48	77.5	2.05	64.2	2.67	83.5	2.59	80.9	2.72	85.0	2.70	84.4
0.0640	5.22	81.5	4.44	69.3	5.29	82.7	5.29	82.7	5.34	83.5	5.36	83.8
0.0960	7.92	82.5	6.94	72.3	7.99	83.4	7.93	82.6	8.13	84.7	8.10	84.3
0.128	10.7	83.6	9.55	74.6	10.7	83.8	10.5	82.0	10.8	84.4	10.8	84.4
0.256	21.4	83.7	20.1	78.4	—	—	—	—	—	—	—	—
0.384	32.0	83.4	—	—	—	—	—	—	—	—	—	—
0.521	43.6	83.6	41.4	80.8	—	—	—	—	—	—	—	—

Gelatin would be a favorable substance in this respect because it does not show such a desorption wave. It has been mentioned already that under certain conditions gelatin may combine chemically with some metal ions. As a typical example, results obtained with copper in ammoniacal medium are shown in Table I, together with results obtained when gelatin of high isoelectric point and polyacrylamide were used instead of ordinary gelatin. It is seen that with ordinary gelatin i_1/C increases markedly with concentration, the effect being much more pronounced with 0.04% than with 0.01% gelatin.

Gelatin of high isoelectric point yielded much better results than ordinary gelatin, as was expected from the fact that the pH of the ammoniacal medium is closer to the isoelectric point of the former than to that of ordinary gelatin. Gelatin of high isoelectric point is useful for the suppression of maxima at the RDME in the electrolysis of ammoniacal copper solutions, but for general purposes polyacrylamide has been found much preferable. This substance does not combine with metals or hydrogen ions and is not desorbed over the entire potential range in neutral, acidic and basic media. Its aqueous solution is perfectly clear and stable and no excessive foaming takes place when nitrogen is passed through.

It is possible to estimate the number of moles of copper bound to a unit quantity of gelatin under our experimental conditions. A plot of i_1 against concentration of copper in the presence of 0.04% gelatin yields a curve (curve II in Fig. 1). Straight line I is obtained when no copper is bound, as was actually found with polyacrylamide as suppressor. If the compound formed by the interaction between copper and gelatin were not dissociated, line II should be straight and not pass through the origin, as represented by the broken line in Fig. 1. The curved part of line II indicates that the compound is appreciably dissociated when the concentration of copper is small. The amount of copper equivalent to a unit amount of gelatin can be estimated from the concentration, C_0, found by extrapolating the apparently straight part of curve II and the gelatin concentration in the experiment. The relation thus found under our experimental conditions for ordinary gelatin was of the order of $2 \cdot 10^{-5}$ mole of copper bound per one gram of gelatin. No effort has been made to find a more exact relation, which would require a further study.

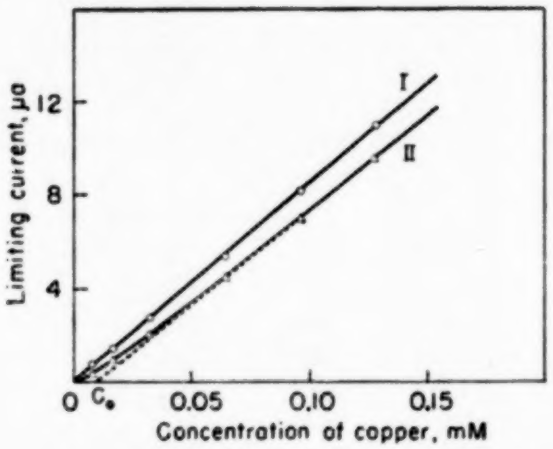

Fig. 1. Limiting current *vs.* concentration of Cu(II) in 0.1 *M* ammonia plus 0.1 *M* ammonium nitrate. (Electrode 2). I, Polyacrylamide (0.01%); II, gelatin (0.04%).

Residual current

Although residual currents at the RDME are a few times greater than those at the DME, their magnitude is small enough to carry out trace determinations at the RDME with reasonable accuracy. Reproducibility of residual current measurements was investigated at electrode 2 with solutions of 0.1 *M* nitric acid and 0.1 *M* potassium chloride both in the presence of 0.01% polyacrylamide. The current was measured with a Sargent Polarograph Model XXI, the sensitivity dial being set at 0.01 μA/mm. The determination was repeated three times with solution prepared separately for each series of measurements. The average values and the average deviations of single measurements at various potentials are shown in Fig. 2 (curves A and B).

Precision of the residual current measurement was better than ± 0.02 μA at potentials more positive than —1.5 V. At more negative potentials it was increased to ± 0.04 μA.

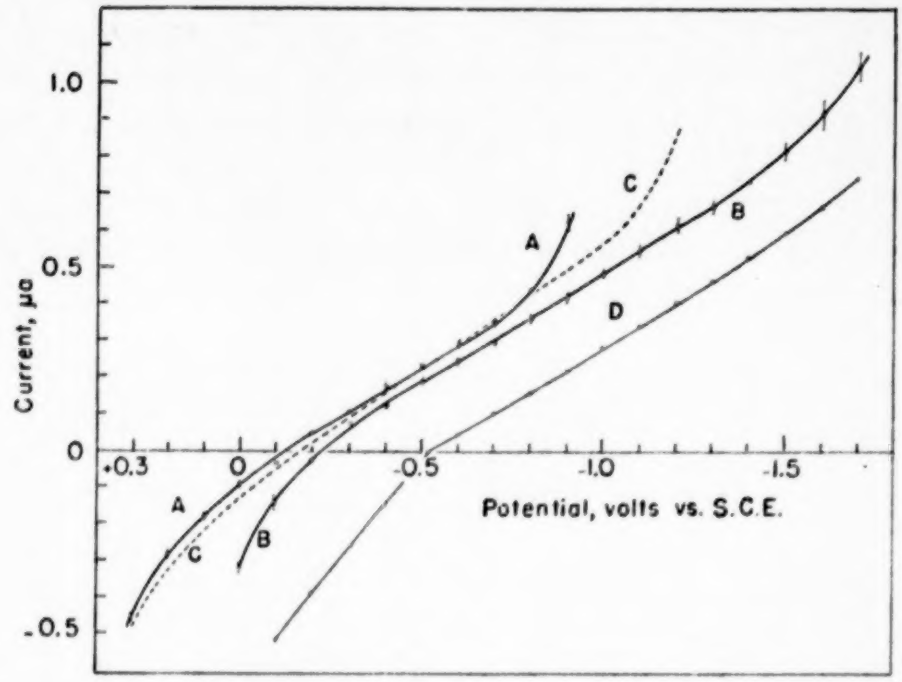

Fig. 2. Residual current–potential curves at electrode 2. A, 0.1 M HNO_3; B, 0.1 M KCl; C, 0.1 M $NaClO_4$ plus 0.001 M $HClO_4$ (all in the presence of 0.01% polyacrylamide); D, calculated condenser current in 0.1 M KCl.

The residual current at the RDME as well as that at the DME is considered to be composed of two components; namely, condenser current and faradaic current. The condenser current at the DME can be calculated from the capacity of the electrical double layer at the mercury-solution interface with the aid of the equation[5]:

$$i_c = 0.0085\, k m^{2/3} t^{-1/3} (E_{\max} - E) \quad \ldots\ldots\ldots\ldots \quad (5)$$

where i_c is the average condenser current in μA, k the capacity of the double layer in microfarads per cm², $E_{\max}$ the potential at the electrocapillary zero in V and E the actual potential of the mercury drop in the experiment. As the condenser current should not be affected by the rotation of the electrode, the above equation is applicable to the RDME as long as the mercury drop can be assumed to be a sphere. Line D in Fig. 2 was obtained by plotting the values calculated by using this equation. The value of k was assumed to be equal to 22 and 46 microfarads per cm² at the negative and positive sides of $E_{\max}$ respectively. These values are the capacity in 0.1 M potassium chloride in the *absence* of an adsorbed layer of surface active substances[5]. The presence of such an adsorbed layer at the interface can change the actual capacity, but this variation may be assumed to be very small, as is evidenced by the recent result of BRESLE[6] that the capacity calculated from his measurements of instantaneous residual currents in 0.1 M potassium chloride in the presence of 0.09% gelatin was 19.7 ± 0.2 microfarads per cm² at —0.94 V *vs.* a silver anode. The calculated condenser current-potential curve (line D in Fig. 2) is composed of two straight lines, which interesect at the isoelectric point. The line on the negative side is essentially straight until a potential of —1.5 V and then starts to curve upward. It is interesting to note that the experimental curve B is practically parallel to the theoretical curve D between $E_{\max}$ (—0.52 V *vs.* S.C.E.) and —1.5 V. The difference between these two curves is undoubtedly due to the presence of impurity (or impurities) reduced at a potential more positive than E_{max}.

It is worth notice that all of the experimental curves given in Fig. 2 are a linear function of the potential between —0.2 or —0.3 V and the potential where hydrogen ion or the supporting electrolyte begins to be reduced. This is true only when the surface active substance is not desorbed. If it is desorbed at a certain potential, the slope of the residual current curve changes at this potential. For practical purposes it is generally desirable to determine the residual current with a solution containing only the supporting electrolyte and the surface active substance. However, the residual current within the range of potentials mentioned above may be estimated with a reasonable accuracy by linear extrapolation of the residual current section of a current–potential curve. It should be realized that this extrapolation procedure is applicable only within the range of potentials in which the residual current changes linearly with the potential.

Reproducibility of the limiting current measurement

Table II illustrates the reproducibility of the measurement of the limiting current at the RDME of a single constituent at various potentials between + 0.3 and —1.8 V *vs.* S.C.E. The current was measured with a Sargent Polarograph Model XXI by setting the sensitivity dial at 0.4 μA/mm. In order to keep the residual current small in com-

TABLE II

REPRODUCIBILITY OF THE LIMITING CURRENT MEASUREMENT (CORRECTED FOR RESIDUAL) AT VARIOUS POTENTIALS AND ACCURACY OF THE ESTIMATION OF THE LIMITING CURRENT BY THE DROP TIME METHOD (METHOD A)

(Electrode No. 2)

Applied potential volt vs. S.C.E.	*t sec*	*i_l observed (corrected for residual) μA*					*i_l calcd. μA*	*Dev. from mean (%)*
		1	*2*	*3*	*Mean*	*Aver. Dev. (%)*		
(0.2 m*M* Hg^{+2} in 0.1 *M* HNO_3 and 0.01% polyacrylamide)								
+0.3	3.70	19.3	19.0	19.2	19.17	0.6	18.9	—1.4
+0.1	3.99	20.4	20.1	20.3	20.27	0.5	20.1	—0.8
—0.1	4.18	21.2	20.8	21.2	21.07	1.5	21.0	—0.3
—0.3	4.31	21.4	21.2	21.5	21.37	0.5	21.5	+0.6
—0.5	4.34	21.9	21.4	21.6	21.63	0.8	21.6	—0.1
—0.6	4.36	21.8	21.5	21.8	21.70	0.6	21.70*	—
—0.8	4.30	21.8	21.4	21.8	21.67	0.8	21.5	—0.8
—1.0	4.20	21.4	21.3	21.4	21.37	0.2	21.0	—1.7
(0.5 m*M* Tl^{+} in 0.1 *M* KCl and 0.01% polyacrylamide)								
—0.8	4.27	35.9	35.8	35.8	35.83	0.1	35.83*	—
—0.9	4.23	35.5	35.2	35.4	35.37	0.3	35.6	+0.7
—1.1	4.02	34.7	34.4	34.4	34.50	0.4	34.1	—1.1
—1.3	3.84	33.5	33.2	33.5	33.40	0.4	32.8	—1.8
—1.5	3.61	31.7	31.8	31.8	31.77	0.1	31.1	—2.1
—1.7	3.32	30.0	29.3	29.4	29.57	1.0	29.0	—1.9
—1.8	3.15	28.8	27.8	28.4	28.33	1.3	27.8	—1.9

* The mean values of the limiting current at these potentials were used to calculate the limiting currents at other potentials.

parison with the true limiting current, relatively high concentrations of metal ions were used. The agreement between three separate measurements was entirely satisfactory, the average deviation of a single measurement from mean being smaller than ± 1.5% over the entire range of potentials investigated (see the third column from the right end of Table II).

It is obvious that when the ratio of true limiting current to residual current is smaller, the possible error in the determination of the former becomes greater. Assuming that the possible error in the measurement of the total current, *i.e.* the sum of true limiting current and residual current, is ± 1.5% and that in the residual current measurement ± 0.02 μA when its magnitude is 0.50 μA, the minimum value of the limiting current to keep the possible error in its determination within ± 2% can be calculated from the formula:

$$\sqrt{0.015^2(i_1 + 0.50)^2 + 0.02^2}/i_1 < 0.02$$

Solving this inequality, we obtain $i_1 > 2.4$ μA. This implies that under the above conditions the limiting current measurement with an error less than ± 2% is possible if the concentration of the species to be analyzed is such that its limiting current corrected for the residual current is greater than 2.4 μA. When the residual current is 0.20 μA where the average deviation is about ± 0.01 μA, the determination with an error less than ± 2% is possible if the limiting current is greater than about 1 μA. These calculations show that satisfactory determinations of a single component are possible with a RDME at concentrations as low as 1 to $2 \cdot 10^{-5} M$.

Analysis of mixtures of two reducible substances

In analyses of mixtures of two reducible constituents, the accuracy of the determination of a constituent which produces the second wave is greatly dependent upon the accuracy of the estimation of the current which the constituent producing the

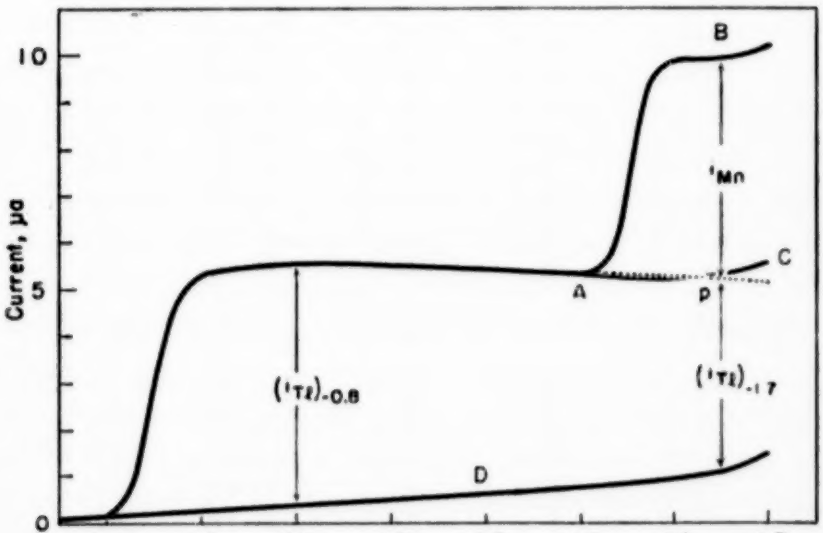

Fig. 3. Current–potential curve (not corrected for the residual current) of a mixture of $7.65 \cdot 10^{-5} M$ thallium and $7.79 \cdot 10^{-5} M$ manganese in $0.1 M$ KCl in the presence of 0.01% polyacrylamide (Electrode 2). AC, thallium alone; AP, extrapolation line (broken line); D, residual current.

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first wave would have at the potential where the limiting current of the second wave is measured. As an example, current–potential curves obtained with a mixture of thallium and manganese are shown in Fig. 3 (not corrected for the residual current) and in Fig. 4 (corrected for the residual current). The limiting current of thallium $(i_{\text{Tl}})_{-0.8}$, is measured, for example at —0.8 V, after correcting for the residual current, while the sum of the limiting currents of thallium and manganese is measured at, for example, —1.7 V. The manganese current is found after correcting this total current for the residual current and for the limiting current, $(i_{\text{Tl}})_{-1.7}$, which thallium would have at this potential. It is evident from this example that the accuracy of the estimation of $(i_{\text{Tl}})_{-1.7}$ is an important factor as far as the accuracy of the determination of manganese is concerned. It becomes increasingly important with decreasing ratio of i_{Mn} to $(i_{\text{Tl}})_{-1.7}$.

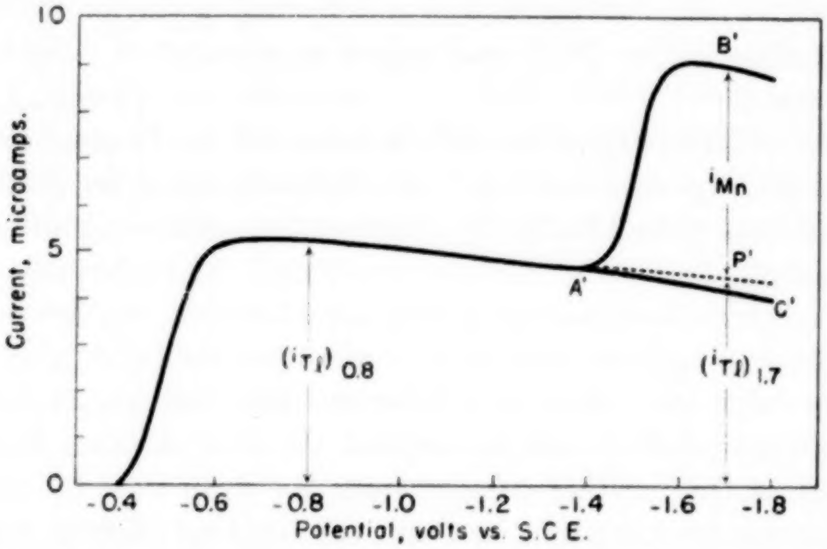

Fig. 4. Current–potential curve (corrected for the residual current) constructed from Fig. 3. A'C', thallium alone; A'P', extrapolation line.

As has been mentioned already, the limiting current at the RDME is affected by the potential to a significant extent and consequently, in the above example, $(i_{\text{Tl}})_{-1.7}$

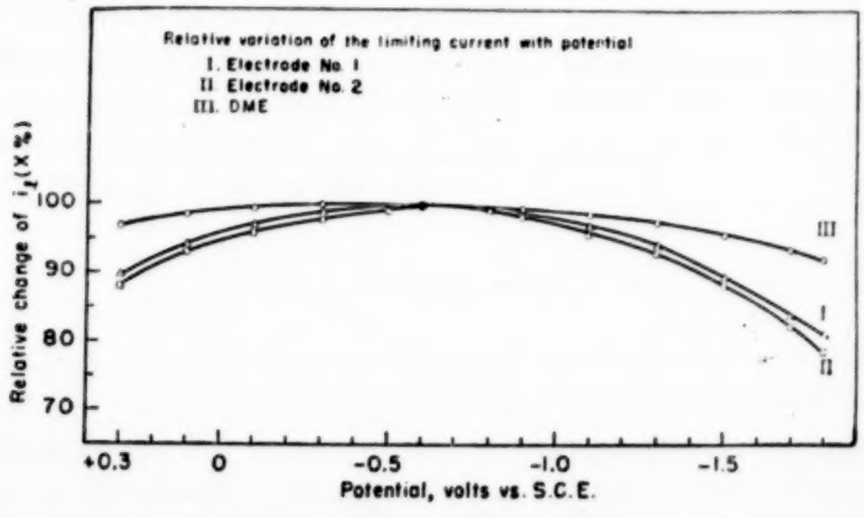

Fig. 5. Relative variation of the limiting current with potential. I, Electrode 1; II, Electrode 2; III, DME.

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is considerably different from $(i\tau^{l})_{-0.8}$ as can be seen from Fig. 4. A clearer and more general illustration is given in Fig. 5 in which the relative change of the limiting current with the potential at electrodes 1 and 2 and that of the diffusion current at a DME are plotted. These curves were constructed from experimental data obtained with solutions of thallium in 0.1*M* potassium chloride and of mercury(II) in 0.1*M* nitric acid both in the presence of 0.01% polyacrylamide. The value at —0.6 V was arbitrarily taken as 100 for each of the curves. As was anticipated, deviation from 100 at various potentials was smallest at the DME and largest at electrode 2, which was more sensitive than electrode 1.

At the DME (curve III in Fig. 5) the diffusion current can be assumed to be constant within the potential range from zero to —1.0 V. Similarly at the RDME the limiting current can be assumed to be practically constant between —0.3 and —0.8 V (curves I and II). Accordingly, there is no difficulty encountered within this potential range in the analysis of mixtures (see example 4, Fig. 10). However, in other potential regions, it is necessary to have a suitable method for estimating the limiting current at a given potential from its value (or values) at a different potential (or potentials). Below we discuss various methods which can be applied for this purpose. Methods A and B consist in calculating the limiting current from the drop time by using relation (3) or from the predetermined relation between the limiting current and potential (*cf.* curves in Fig. 5). These calculation methods are generally applicable over the entire potential range and give accurate results even under extreme conditions. Methods C and D consist in extrapolating an apparently linear part of limiting current–potential curves corrected or not corrected for the residual current. These extrapolation methods have only a limited applicability within certain potential ranges.

Method A. The exponent, a, in equation (3) is determined empirically for the particular electrode employed under given experimental conditions. This can be done by measuring the limiting current over a wide range of potentials of a solution of a metal which in general is reduced at the positive side of the electrocapillary zero potential; *e.g.* thallium in potassium chloride, copper(II) in ammonium nitrate plus ammonia or mercuric chloride in potassium nitrate etc. in the presence of 0.01% polyacrylamide. The concentration of the metal need not be known. The value of a is found as the slope of the plot of log i_1 (corrected for the residual current) *vs.* log t. It should be understood that, in a strict sense, this plot should not give a straight line nor should the slope be the same for ions with different diffusion coefficients, as is evident from equation (1). However, under experimental conditions, relation (3) holds so closely that the

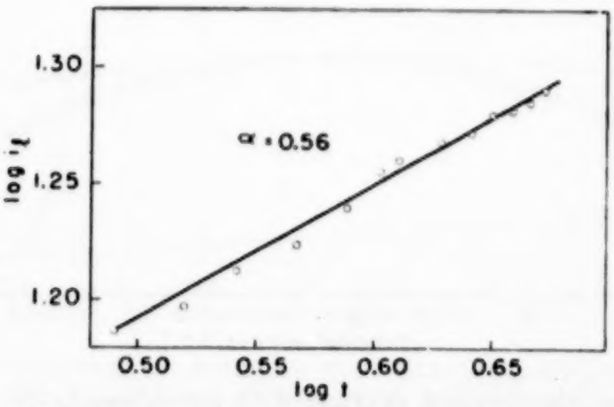

Fig. 6. Determination of a of electrode 1. (0.4 m*M* Tl^+ in 0.1*M* KCl and 0.01% polyacrylamide).

plot yields a straight line whose slope is practically the same for various metal ions. Examples of such $\log i_1 - \log t$ plots at electrodes 1 and 2 are shown in Figs. 6 and 7. In the example of a mixture of thallium and manganese illustrated in Figs. 3 and 4, the limiting current of thallium at —1.7 V can be calculated from the value at —0.8 V by using the relation:

$$(i_{\mathrm{Tl}})_{-1.7} = (i_{\mathrm{Tl}})_{-0.8}(t_{-1.7}/t_{-0.8})^{a} \quad \ldots\ldots\ldots\ldots\ldots \quad (6)$$

where $t_{-1.7}$ and $t_{-0.8}$ are the drop times at —1.7 and —0.8 V respectively.

The order of magnitude of the error in the estimation by this method does not exceed 2% as indicated in the last column of Table II. This column also shows that practically all of the deviations have a negative sign. As is obvious from the fact that the experimental points in the $\log i_1 - \log t$ plot are scattered on both sides of the best-fitted straight line, the direction of the deviation of calculated from observed values can become either mostly positive or negative, unless the point taken as a reference in the calculation [$(i_{\mathrm{Tl}})_{-0.8}$ in the above example] happens to be on the straight line.

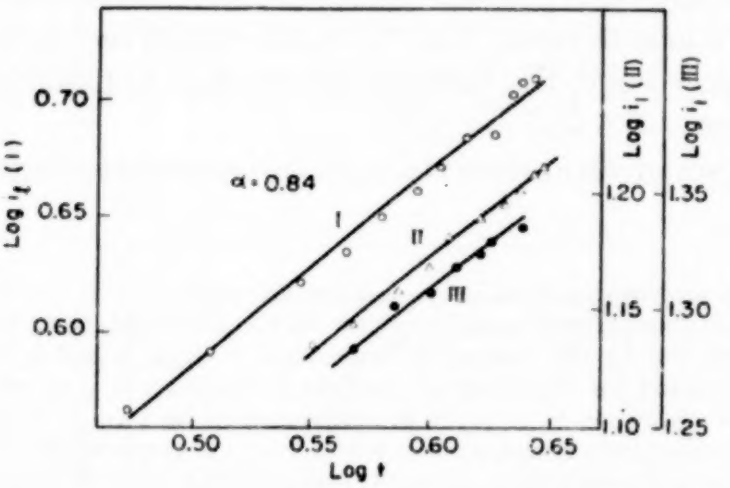

Fig. 7. Determination of a of electrode 2. (I, 0.08 mM Tl^+ in 0.1M KCl; II, 0.2 mM Cu(II) in 0.1M NH_4NO_3 and 0.1M NH_4OH; III, 0.2 mM Hg(II) in 0.1M HNO_3; all in the presence of 0.01% polyacrylamide).

Method B. The curve obtained by plotting the relative variation of the limiting current with potential can be made use of directly for the present purpose. For example, the limiting current of thallium at —1.7 V, $(i_{\mathrm{Tl}})_{-1.7}$, is obtained from the value measured at —0.8 V, $(i_{\mathrm{Tl}})_{-0.8}$, by using the relation:

$$(i_{\mathrm{Tl}})_{-1.7} = (i_{\mathrm{Tl}})_{-0.8}\,(X_{-1.7}/X_{-0.8}) \quad \ldots\ldots\ldots\ldots \quad (7)$$

where $X_{-1.7}$ and $X_{-0.8}$ are the relative values of the limiting current read on the ordinate (Fig. 5) at —1.7 and —0.8 V respectively. As is evidenced by the experimental fact that the slope of the $\log i_1 - \log t$ plot is practically the same for various ions at a given electrode, the relative variation of the limiting current with potential should also be the same for different ions. Naturally this is not strictly true if the solution contains capillary active ions or compounds which shift the electrocapillary zero potential. With this exception, method B is actually simpler than method A, because the former does not require the determination of the drop time.

Method C. The limiting current plateau of the first constituent of the current-potential curve corrected for the residual current (*cf.* Fig. 4) is extrapolated linearly to the potential where the second constituent is determined. In the example of a mixture of thallium and manganese, for instance, i_{Mn} is determined by subtracting the current read on the ordinate at point P′ from the total current (the value at B′ in Fig. 4) corrected for the residual current.

Method D. A similar extrapolation is made using the current-potential curve not corrected for the residual current (*cf.* Fig. 3). With this method it is unnecessary to know the residual current in estimating the concentration of the second constituent.

In applying methods C or D, it should be realized that within no potential region limiting current-potential curves at the RDME are truly straight as shown in Fig. 5. Naturally, therefore, the extrapolation should be made within as narrow a potential range as possible. It is also obvious that the extrapolation methods can be successfully applied only in a region where the limiting current does not change very rapidly with potential, *e.g.* between —0.8 and —1.5 V.

Examples of analyses of various mixtures of two reducible substances are illustrated below.

Example 1. Thallium and manganese in potassium chloride.

This is an example of an extreme case in which methods A and B give more accurate results than the graphical methods. In the example illustrated in Figs. 3 and 4, the limiting current of thallium at —0.8 V corrected for the residual current of thallium is 5.19 μA. Applying method A, the limiting current of thallium at —1.7 V is calculated to be $5.19 \times (3.36/4.27)^{0.84} = 4.24$ μA, where 4.27 and 3.36 are the drop times at —0.8 and —1.7 V respectively. This value agrees with the limiting current 4.20 μA which was actually measured at —1.7 V with a solution containing thallium alone. Using method B, $(i_{Tl})_{-1.7}$ is calculated to be $5.19 \times (82.5/99.5) = 4.30$ μA, where 82.5 and 99.5 are the relative values of the limiting current at —1.7 and —0.8 V found from curve II in Fig. 5. This value of the limiting current also agrees satisfactorily with the expected value of 4.20 μA. With method C (Fig. 4), $(i_{Tl})_{-1.7}$ is found to be 4.40 μA, which corresponds to an error of + 5%. This higher value was to be anticipated from the rapid decrease of the drop time and hence of the limiting current at these negative potentials (see Figs. 4 and 5). It is evident from Fig. 3 that method D using the current-potential curve not corrected for the residual current gives an erroneous result at these negative potentials because of the noticeable reduction of the supporting electrolyte.

For a further confirmation of the superiority of methods A and B to the extrapolation methods in this case, an unknown mixture of thallium and manganese was analyzed by the various methods. The analyses were carried out in triplicate with electrode 2 in the presence of 0.01% polyacrylamide. The results are given in Table III, which shows that even under this extreme condition where the extrapolation methods are not reliable, methods A and B yield results accurate and precise within 2%, while methods C and D yield values for manganese which are equally precise, but much less accurate.

Example 2. Mercury(II) and bismuth(III) in nitric acid.

This is another example of an extreme case, but at the positive side of the isoelectric point in which only methods A and B give acceptable results. Current-potential curves obtained with a mixture of these metals are shown in Fig. 8.

Extrapolations were made starting at +0.15 V on both current-potential curves, corrected and not corrected for the residual current. The extrapolated lines I'_e and II'_e deviate considerably from curves I′ and II′ obtained with a solution of the same concentration of mercury alone. With method C, the limiting current of mercury read on the extrapolation line II'_e at —0.3 V was 1.86 μA, as compared to 1.78 μA which was found with mercury alone. The total current corrected for the residual current at this potential was 3.00 μA. Thus the limiting current of bismuth found by method C becomes 1.14 μA, while the value found with a solution containing bismuth alone was 1.21 μA. This error of —6% is significant. With method D the limiting current of bismuth at —0.3 V was derived to be 1.01 μA, which corresponds to an error of about —17%. This large negative error is accounted for by the fact that the steep variation of the residual current at potentials more posi-

TABLE III

ANALYSIS OF A MIXTURE OF THALLIUM AND MANGANESE

(The sample contained $8.38 \cdot 10^{-5} M$ Tl^+ and $4.08 \cdot 10^{-5} M$ Mn^{+2}). i_1/C values for Tl^+ at —0.8 V and for Mn^{+2} at —1.7 V were 68.8 and 61.0 μA per mM respectively.

Expt No.	$(i_{Tl})_{-0.8}$ *(corrected for* i_r*), μA*	*Total current at —1.7 V*		i_{Mn} *measured at —1.7 V, μA method*			
		not corrected for i_r*, μA*	*corrected for* i_r*, μA*	*A**	*B***	*C*	*D*
1	5.68	8.26	7.19	2.46	2.50	2.32	2.68
2	5.66	8.28	7.21	2.50	2.54	2.36	2.71
3	4.75	8.28	7.21	2.43	2.47	2.31	2.66
Av.	5.69 ± 0.03			2.46 ± 0.02	2.50 ± 0.02	2.33 ± 0.02	2.68 ± 0.02
Tl^+ found =	(8.27 ± 0.04) $\cdot 10^{-5} M$ (—1.3%)	Mn^{+2} found = $(\cdot 10^5 M)$		4.03 ± 0.03 (—1.2%)	4.10 ± 0.03 (+0.5%)	3.82 ± 0.03 (—6.4%)	4.39 ± 0.03 (+7.6%)

* Drop times at —0.8 and —1.7 V were 4.38 and 3.44 sec respectively.
** (i_1 at —1.7 V)/(i_1 at —0.8 V) = 0.825 (computed from Fig. 5).

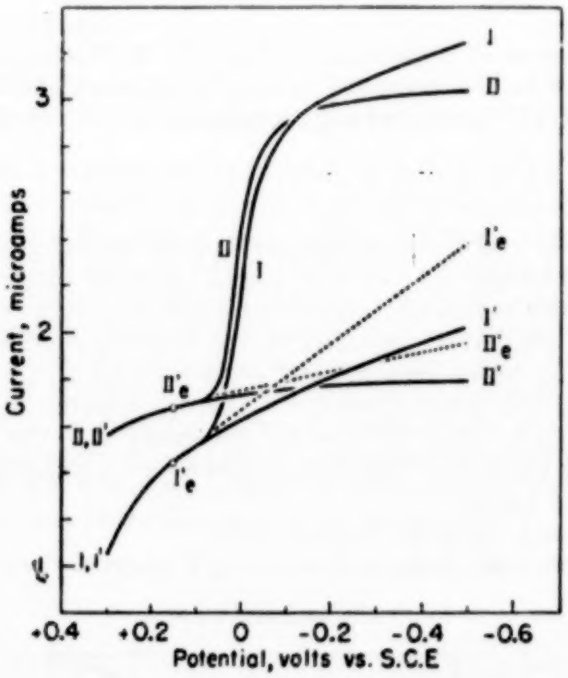

Fig. 8. Current–potential curves of a mixture of $1.54 \cdot 10^{-5} M$ bismuth and $1.90 \cdot 10^{-5} M$ mercury in $0.1 M$ HNO_3 in the presence of 0.01% polyacrylamide (electrode 2). I, I′, not corrected for the residual; II, II′, corrected for the residual; I′, II′, mercury alone; I'_e, II'_e, extrapolation lines.

tive than zero volt (line A in Fig. 2) is superimposed on the steep change of the true limiting current at these potentials.

With method A, the limiting current of mercury at —0.3 V is calculated from the value of 1.64 μA measured at +0.2 V to be $1.64 \times (4.31/3.82)^{0.84} = 1.81$ μA, which is in good agreement with the value of 1.78 μA which was found with a solution of mercury alone. Subtracting this value from the total current of 3.00 μA, we obtain 1.19 μA for the bismuth current as compared to the value of 1.21 μA measured with a solution of bismuth alone. With method B the bismuth current at —0.3 V is calculated to be 3.00-1.64 (98.6/91.0) = 1.22 μA. Thus in this case, as well as in example 1, methods A and B are recommended although method C gives reasonable results, even in these extreme cases.

Example 3. Thallium and iodate in potassium chloride and borax.

Current–potential curves obtained with a mixture of these ions are shown in Fig. 9. The limiting and the apparent limiting currents of thallium vary in a linear way with potential between —0.8 and —1.2 V on both current–potential curves, corrected and not corrected for the residual current. At —1.5 V where the iodate limiting current was measured, the extrapolated lines I'_e and II'_e do not deviate significantly from curves I′ and II′ obtained with thallium alone. For this reason the extrapolation methods, C and D, yield almost equally satisfactory results as methods A or B. The limiting current of iodate at —1.5 V found by using methods C and D was 4.22 and 4.21 µA respectively, while the value obtained with a solution containing iodate alone was 4.32 µA; thus the error is only —2.5%. With method A the limiting current of thallium at —1.5 V is calculated, from the value of 4.78 µA measured at —0.8 V, to be $4.78 \times (3.65/4.28)^{0.84} = 4.18$ µA. Subtracting this value from the total current of 8.54 µA (corrected for the residual current), the iodate current becomes 4.36 µA, which is in good agreement with the expected value of 4.32 µA. With method B the limiting current of iodate becomes $8.54 - 4.78 \times (88.6/99.5) = 4.26$ µA, which also agrees with the expected value.

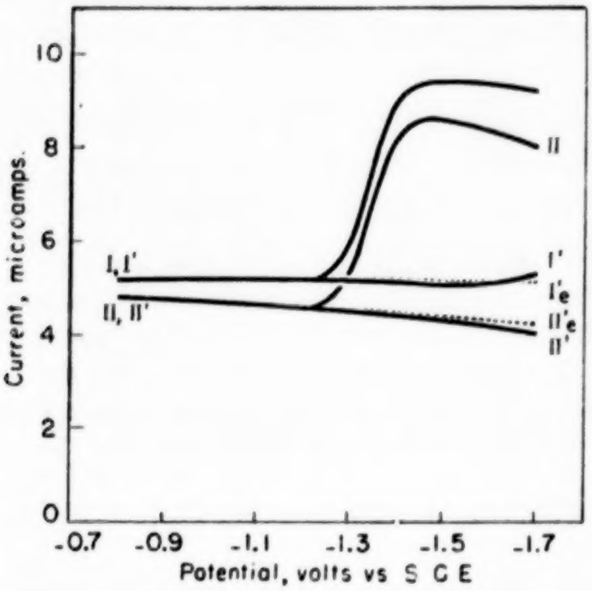

Fig. 9. Current–potential curves of a mixture of $8.04 \cdot 10^{-5}M$ thallium and $2.00 \cdot 10^{-5}M$ iodate in $0.1M$ KCl plus $0.05M$ borax in the presence of 0.01% polyacrylamide (Electrode 2). I, I′, not corrected for the residual; II, II′, corrected for the residual; I′, II′, thallium alone; I'_e, II'_e, extrapolation lines.

Example 4. Mercury (II) and thallium in nitric acid.

In this example the currents are measured at —0.3 V (mercury) and at —0.7 V (mixture). In

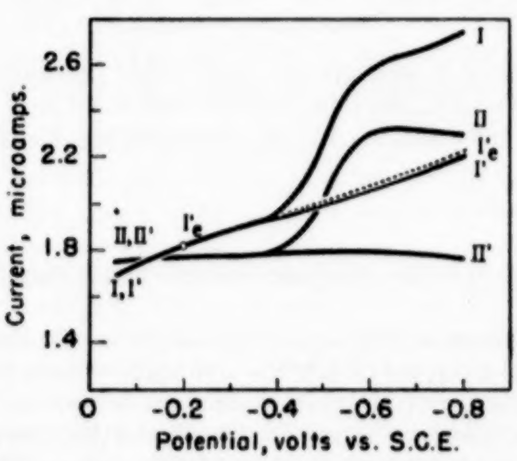

Fig. 10. Current–potential curves of a mixture of $1.90 \cdot 10^{-5}M$ mercury and $0.828 \cdot 10^{-5}M$ thallium in $0.1M$ HNO_3 in the presence of 0.01% polyacrylamide (Electrode 2). I, I′, not corrected for the residual; II, II′, corrected for the residual; I′, II′, mercury alone; I'_e, extrapolation line.

References p. 309

this potential range the limiting current of mercury is essentially constant and the simple graphical method D can be used. Current–potential curves obtained with a mixture of mercury and thallium are shown in Fig. 10.
The limiting current of mercury corrected for the residual current at —0.3 V was 1.77 μA, while at —0.7 V the current observed with a solution of the same concentration of mercury alone was 1.78 μA. The residual current measured in 0.1 M nitric acid changes lineraly between —0.2 and —0.7 V (see curve A in Fig. 2), and a linear extrapolation, which is started at —0.2 V (see I'_e in Fig. 10) on the current-potential curve not corrected for the residual current, should yield an accurate value of the current at —0.7 V (method D). This is substantiated by the over-all agreement of the results obtained by all four methods.

It is concluded from the above examples that, at very positive or very negative potentials where the limiting current changes rapidly with potential, methods A or B must be used, while within the intermediate potential range the simple extrapolation methods give acceptable results. The above examples also show that in the applicable potential range the two extrapolation methods, using current–potential curves corrected or not corrected for the residual current, give practically the same results.

We carried out a few experiments with mixtures of several reducible constituents, *e.g.* copper, cadmium, nickel and zinc in an ammoniacal medium and found that exactly the same principle as for mixtures of two constituents applies to those cases. Results obtained at concentrations of each constituent of the order of $2 \cdot 10^{-5} M$ were of the same degree of accuracy as those obtained at the DME in mixtures twenty times more concentrated in each constituent.

SUMMARY

The use of poylacrylamide is recommended instead of gelatin as an ideal maximum suppressor to be employed with both the rotated dropping mercury electrode (RDME) and conventional dropping electrode (DME). It is retained at the mercury surface over the entire potential range and does not combine with heavy metals. Reproducibility of the measurement of the residual current and that of the limiting current at the RDME were studied, and it was found that accurate determinations of a single constituent ($\pm$ 2%) are possible at concentrations as low as 1 to $2 \cdot 10^{-5} M$. The variation of the limiting current with potential is much greater at the RDME than at the DME. This effect must be considered in the analysis of a mixture of electroactive species at the RDME. Methods have been discussed for making the proper correction for a preceding wave when a limiting current of a mixture of constituents is measured. Because of its high sensitivity and good reproducibility of results, the RDME is recommended for the analysis of solutions containing one or more electroactive species at concentrations less than $10^{-4} M$.

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BACK TITRATION WITH MERCURIC NITRATE IN ALKALINE MEDIUM

VOLUMETRIC ANALYSIS OF BINARY MIXTURES OF THE ALKALINE EARTHS, MAGNESIUM, ZINC AND CADMIUM

by

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In a very recent investigation[1], a moderately acidic solution of mercuric nitrate has proved to be an excellent backtitrant for EDTA solutions in buffered media lying on the alkaline side of pH 8 up to pH 11. The exchange kinetics between mercuric nitrate and the versenates of some metals such as magnesium, barium and strontium were found to be dependent on the buffering capacity of the titration system and consequently upon the pH of the added buffer solutions. The fact that there is no exchange reaction between mercuric nitrate and the versenates of some other metals such as cadmium, zinc and calcium, at any of the above mentioned pH's, suggested that the volumetric analysis of mixtures of two or three of these cations by a simple selection of pH might be feasible. Among the methods cited in the literature for pH-controlled volumetric analysis, the method of BROWN[2] for the simultaneous determination of zinc and magnesium with sodium versenate and Solochrome Black indicator, may be mentioned. The method presented here has the advantages of being rapid, simple and highly precise, since the titrations are performed potentiometrically and the jumps at the equivalence points are sharp enough to be detected.

EXPERIMENTAL

Compounds

All the materials used in this investigation were of the requisite purity. They were the nitrates of mercury, barium, calcium, strontium, zinc, magnesium, cadmium and ammonium.

Solutions

Mercuric nitrate solution. About 16.8 g of the pure salt was dissolved in 1 l of twice distilled water with the aid of 3 ml of conc. nitric acid solution or preferably less if possible. The resulting solution was standardised volumetrically against 0.01 *M* EDTA solution at pH's 8-11. The mean molarity of the mercuric nitrate solution was calculated to be 0.0505.

Buffer solutions. Stock solutions of 1 *M* ammonium nitrate (80 g/l) and 1 *M* ammonium hydroxide (70 ml conc. ammonia/l) were used.

Buffer pH 8 (1 *M*). A suitable volume of 1 *M* NH_4NO_3 solution was transferred to a beaker. The 1 *M* NH_4OH solution was gradually added and the pH was read on a recording pH-meter connected to a glass electrode immersed in the solution mixture.

Buffer pH 9 (0.25 *M*). A 1 *M* solution was prepared as described above. The resulting buffer was diluted with water in the ratio 1:4.

Buffer pH 10 (0.1 *M*). A 1 *M* buffer was prepared and diluted in the ratio 1:10.

Buffer pH 11 (0.1 *M*). To the 0.1 *M* buffer, pH 10, conc. ammonia was gradually added until the pH-meter recorded the desired pH.

Solutions of the alkaline earths, magnesium, zinc and cadmium. 0.01M solutions were prepared by dissolving the calculated amounts in the appropriate volumes of pure water. These solutions were standardised titrimetrically against 0.01M EDTA solution according to the procedures recommended by SCHWARZENBACH[3].

Equipment

A recording pH and potentiometer (type Beckman Automatic Titrator K) was used either for measuring the pH of the buffer solutions with the aid of the glass electrode, or for recording the potentials after each addition of titrant. The titration cell consisted of an amalgamated silver electrode acting as the positive half cell, and the saturated calomel electrode as the other half cell. The surface of the silver amalgam electrode was restored now and then by immersing overnight in a pure mercury pool. A saturated KNO_3 solution was used as a salt bridge for connecting the two half cells. The $Hg(NO_3)_2$ solution was delivered from a 5-ml microburette, the tip of which was kept immersed in the titration mixture during operation. Stirring of the latter was affected by means of a magnetic stirrer.

The titration principle

The results of the previous investigation[1] indicate that the back titration of zinc, cadmium or calcium with mercuric nitrate at pH 8, 9, 10 and 11, proceeds directly to the equivalence points corresponding to the excess versene solutions, whereas with magnesium, barium or strontium at pH 8 and 9, the end-points correspond to the total versene solutions. These results were explained by the exchange reaction between mercuric nitrate and the last-mentioned metals at pH 8 and 9, thus

$$Hg(NO_3)_2 + M^{-2} = Hg^{-2} + M(NO_3)_2$$

where M represents magnesium, barium or strontium. Between pH 10 and 11 the back titration curves of magnesium or strontium showed no deviation from the theoretical end-points corresponding to excess versene solutions. The titration curve of barium at pH 10 showed two small inflections corresponding to a partial exchange reaction, whereas at pH 11 a smooth curve was obtained showing no exchange between barium versenate and mercuric nitrate. Consequently a back titration of any of the three elements zinc, cadmium and calcium in combination with any of the three elements magnesium, barium and strontium seemed possible simply by performing one titration at pH 8 or 9 and another titration of the same constituents at pH 10 or 11.

TABLE I

ANALYSIS OF Mg (0.0101M) + Zn (0.0100M)

Volume ml	*ml T ≡ V** *(a)*	*mV/0.1 ml*	*ml T ≡ Zn* *(2.97—a)*	*M Zn*	
pH 8					
5 Mg + 5 Zn	1.980	35	0.990	0.00999	
5 Mg + 3 Zn	2.380	32	0.590	0.00993	
3 Mg + 5 Zn	1.975	32	0.995	0.01005	
pH 11			*ml T ≡ Mg + Zn*	*ml T ≡ Mg*	*M Mg*
5 Mg + 5 Zn	0.980	67	1.990	1.000	0.01010
5 Mg + 3 Zn	1.375	50	1.595	1.005	0.01015
3 Mg + 5 Zn	1.375	62	1.595	0.600	0.01010

* $T = 0.0505M\ Hg(NO_3)_2$ V = excess 0.01M EDTA.

The procedure applied for the analysis of the above-mentioned two-component mixtures involved transferring the solutions into the titration vessel in the following order: 3-5 ml of each of the metal ion solutions, 15 ml 0.01 M EDTA solution and 40 ml buffer solution. The titration vessel was then transferred to the stirrer and the end-point was traced with the aid of the recording potentiometer. Three synthetic mixtures were always analysed, the first containing 5 + 5, the second 5 + 3 and the third 3 + 5 ml of each of the two metal ion solutions. The results are listed in Tables I to VI.

TABLE II

ANALYSIS OF Mg (0.0101 M) + Cd (0.0101 M)

Volume ml	*ml T ≡ V (a)*	*mV/0.1 ml*	*ml T ≡ Cd (2.97—a)*	*M Cd*	
pH 8					
5 Mg + 5 Cd	1.970	72	1.00	0.0101	
5 Mg + 3 Cd	2.370	37	0.60	0.0101	
3 Mg + 5 Cd	1.970	45	1.00	0.0101	
pH 11			*ml T ≡ Mg + Cd*	*ml T ≡ Mg*	*M Mg*
5 Mg + 5 Cd	0.980	63	1.99	1.00	0.01010
5 Mg + 3 Cd	1.370	53	1.60	1.00	0.01010
3 Mg + 5 Cd	1.365	61	1.61	0.605	0.01018

TABLE III

ANALYSIS OF Ba (0.010 M) + Zn (0.010 M)

Volume ml	*ml T ≡ V (a)*	*mV/0.1 ml*	*ml T ≡ Zn (2.97—a)*	*M Zn*	
pH 8					
5 Ba + 5 Zn	1.980	67	0.990	0.00999	
5 Ba + 3 Zn	2.380	50	0.590	0.00993	
3 Ba + 5 Zn	1.980	49	0.980	0.00999	
pH 11			*ml T ≡ Ba + Zn*	*ml T ≡ Ba*	*M Ba*
5 Ba + 5 Zn	0.990	35	1.980	0.990	0.00999
5 Ba + 3 Zn	1.370	39	1.600	1.00	0.01010
3 Ba + 5 Zn	1.380	52	1.590	0.60	0.01010

The above results (some of which are represented graphically in Fig. 1) show fair agreement in almost all cases between the molarities of the cations as determined by back titration and those determined separately by the direct method.

Attempts to back titrate mixtures of calcium and magnesium, barium or strontium were not successful at the lower pH's. At pH 11, however the titration proceeded to the equivalence points corresponding to both cations with reasonable jumps amounting to *ca.* 65 mV per 0.1 ml of titrant.

TABLE IV

ANALYSIS OF Sr (0.01007*M*) + Zn (0.010*M*)

Volume ml	*ml T ≡ V* *(a)*	*mV/0.1 ml*	*ml T ≡ Zn* *(2.97—a)*	*M Zn*	
pH 8					
5 Sr + 5 Zn	1.985	40	0.985	0.00995	
5 Sr + 3 Zn	2.375	30	0.595	0.01001	
3 Sr + 5 Zn	1.980	36	0.990	0.00999	
pH 11			*ml T ≡ Zn + Sr*	*ml T ≡ Sr*	*M Sr*
5 Sr + 5 Zn	0.983	60	1.987	1.002	0.01012
5 Sr + 3 Zn	1.372	58	1.598	1.003	0.01013
3 Sr + 5 Zn	1.380	62	1.590	0.605	0.01018

TABLE V

ANALYSIS OF Ba (0.010*M*) + Cd (0.0101*M*)

Volume ml	*ml T ≡ V* *(a)*	*mV/0.1 ml*	*ml T ≡ Cd* *(2.97—a)*	*M Cd*	
pH 9					
5 Ba + 5 Cd	1.970	40	1.00	0.01010	
5 Ba + 3 Cd	2.372	41	0.598	0.01006	
3 Ba + 5 Cd	1.973	45	0.997	0.01007	
pH 11			*ml T ≡ Ba + Cd*	*ml T ≡ Ba*	*M Ba*
5 Ba + 5 Cd	0.975	43	1.995	0.995	0.01005
5 Ba + 3 Cd	1.377	47	1.593	0.995	0.01005
3 Ba + 5 Cd	1.375	52	1.595	0.598	0.01006

TABLE VI

ANALYSIS OF Sr (0.01007*M*) + Cd (0.0101*M*)

Volume ml	*ml T ≡ V* *(a)*	*mV/0.1ml*	*ml T ≡ Cd* *(2.97—a)*	*M Cd*	
pH 8					
5 Sr + 5 Cd	1.973	47	0.997	0.01007	
5 Sr + 3 Cd	2.369	40	0.601	0.01011	
3 Sr + 5 Cd	1.970	48	1.00	0.01010	
pH 11			*ml T ≡ Sr + Cd*	*ml T ≡ Sr*	*M Sr*
5 Sr + 5 Cd	0.975	60	1.995	0.998	0.01008
5 Sr + 3 Cd	1.365	76	1.605	1.004	0.01014
3 Sr + 5 Cd	1.370	67	1.600	0.600	0.01010

References p. 314

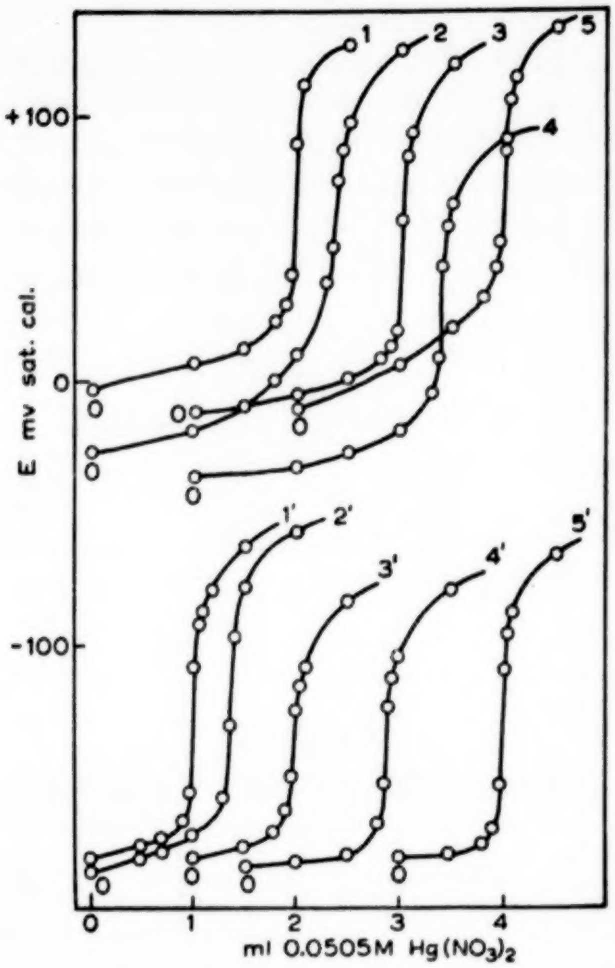

Fig. 1. Back titrations with mercuric nitrate.

1. 5 ml 0.0101 *M* Mg + 5 ml 0.0101 *M* Cd + 15 ml 0.01 *M* EDTA solution, pH 8.
2. 5 ml 0.0101 *M* Mg + 3 ml 0.0101 *M* Cd + 15 ml 0.01 *M* EDTA solution, pH 8.
3. 5 ml 0.0100 *M* Ba + 5 ml 0.0100 *M* Zn + 15 ml 0.01 *M* EDTA solution, pH 8.
4. 5 ml 0.0100 *M* Ba + 3 ml 0.0100 *M* Zn + 15 ml 0.01 *M* EDTA solution, pH 8.
5. 5 ml 0.01007 *M* Sr + 5 ml 0.0101 *M* Cd + 15 ml 0.01 *M* EDTA solution, pH 8.

1', 2', 3', 4', and 5': the same as 1-5, at pH 11.

SUMMARY

Mercuric nitrate has proved to be suitable for the back titration of the excess amount of EDTA remaining in solution when this compound has reacted quantitatively either with zinc or cadmium in the presence of one of the three elements barium, strontium and magnesium at pH 8 or 9, or with both cations at pH 11. Advantage is taken of this behaviour for analysing binary mixtures of the above mentioned cations by back titration at lower and higher pH's. The end-points are detected potentiometrically, reasonable jumps being obtained; the agreement with the theoretical end-points is satisfactory.

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MERCURIMETRIE ZUR CHLORIDBESTIMMUNG

von

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Silbermethoden sind heutzutage das Übliche zur Bestimmung der Chloride. Bei Benutzung von Diphenylcarbazon als Indikator kann man eben so genau, aber schneller und viel billiger mit Mercurinitrat titrieren. Besonders bequem und ökonomisch wird dabei das Verfahren wenn man von gelben Quecksilberoxyd ausgeht und dieses durch Auflösen in Salpetersäure in das Nitrat umwandelt.

Herstellung der Titrationslösung

Das Mercurinitrat enthält meist basische Oxyde und kann daher nicht durch direkte Abwägung zur Herstellung der Titrationslösung benutzt werden. Man nimmt daher 10.83 g Quecksilberoxyd, versetzt es mit etwas Wasser und drei bis vier ml konzentrierter Salpetersäure wodurch sofortige Lösung eintritt. Durch Auffüllen mit Wasser auf ein Liter erhält man die 0.1 N Mercurinitratlösung. Wenn das Quecksilberoxyd rein war erübrigt sich eine Kontrolle. Andernfalls kann man diese mit 0.1 N Natriumchloridlösung ausführen.

Zur Titration benötigte Reagentien

1) 0.1 N Mercurinitratlösung
2) Diphenylcarbazonlösung 0.5% in Alkohol
3) Salpetersäure in einem Tropffläschen.

Ausführung der Titration

Diese macht man in saurer Lösung und muss daher bei neutralen Lösungen nach dem Zusatz von zehn Tropfen Indikatorlösung zu 250 ml ein bis drei Tropfen Salpetersäure zugeben. Andernfalls würde bei geringem Chloridgehalt die im Reagens anwesende Säuremenge nicht genügen und das Diphenylkarbazon die violette Farbe schon vor dem Umschlag zeigen.

Man lässt die Mercurinitratlösung zulaufen bis Umschlag nach rosa-violett eintritt.

Empfindlichkeit der Reaktion

Auf 250 ml Lösung genügen 0.05 ml Überschuss an Mercurinitratlösung um eine deutlich violette Färbung zu geben. Es erübrigt sich daher Tabellen mit Resultaten zu geben; statt dessen bringen wir Hinweise auf die Anwendungsgebiete und einige Einzelheiten der Reaktion.

Alle farblosen und ionisierten Chloridlösungen lassen sich mit Mercurinitrat titrieren, wobei die Menge an Säure in der Lösung nicht kritisch ist. Auch Kupferchlorid lässt sich titrieren, nicht aber Eisenchlorid in dessen Gegenwart ein Umschlag ausbleibt. Sehr gut lassen sich reine Salzsäurelösungen titrieren, wodurch man ein bequemes Mittel zur Hand hat diese Säure in einfachster Weise einzustellen.

Vergleichen wir nun diese Methode mit den beiden nach MOHR und nach VOLHARD. Der Umschlag in der sauren Lösung ist wesentlich schärfer, als der in neutraler, da kein Niederschlag eintritt. Phosphate und Karbonate sind nicht mehr von Einfluss auf das Ergebnis und man braucht nicht zu neutralisieren. Noch grösser ist der

Vorteil der Rhodanmethode gegenüber, da man jetzt nicht mehr zwei aufeinander eingestellte Lösungen benutzen muss sondern mit einer allein auskommt. Es geht natürlich viel schneller und einfacher und es werden manche Fehlerquellen vermieden. Ein besonderer Vorzug ist, dass die Lösung keine Flecke hinterlässt und nicht lichtempfindlich ist, so dass man mit farblosen Büretten arbeiten kann. Sie ist natürlich beliebig lange haltbar und auch der Indikator zeigt in den ersten vier Monaten keine Veränderung in der alkoholischen Lösung. Von Interesse ist auch die ausserordentliche Ökonomie des Verfahrens. Man kann rechnen dass Titrationen dieser Art nur ein viertel von dem kosten, was man bei Benutzung von Silbernitrat aufwenden müsste. Bei den Millionen von Chloridbestimmungen die in der Technik und für Harn und Blutanalysen ausgeführt werden ist dies sicher auch ein Faktor von Interesse.

In unserem Labor titrieren wir alle Harne nach diesem System. Sera lassen sich vorzüglich nach Ausfällen des Eiweisses mit Alkohol titrieren.

DANK

Das Diphenylkarbazon wird von der Chemischen Fabrik Siegfried, Zofingen, in den Handel gebracht der wir unseren Dank für das freundlichst übersandte Muster aussprechen. In die U.S.A. wird es auch von der Firma Eastman, Rochester, hergestellt.

ZUSAMMENFASSUNG

Titration von Chloriden mit Mercurinitrat und Diphenylkarbazon ist eben so genau wie mit Silbernitrat, aber bequemer und viel ökonomischer.

SUMMARY

Titration of chlorides with mercuric nitrate and diphenylcarbazone is just as accurate as with silver nitrate, but more economic and more convenient.

Eingegangen, den 16. Juli 1957

THERMOLYSIS OF THORIUM PRECIPITATES

III. SALTS OF ORGANIC ACIDS

by

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This is the third in a series of papers on the investigation of the thermal stability of the thorium precipitates with organic acids[1,2]. The precipitates studied in this investigation are the thorium compounds with tannic (digallic)[3], 5-bromo-salicylic[4], 5-nitrosalicylic[4], 1-hydroxy-2-naphthoic[5], phenyl-glycine-*o*-carboxylic[6], phenylpropionic[7], acetyl-*o*-salicylic[8], phenoxyacetic[3], 2,4,5-trichlorophenoxyacetic[9], and 2,2′-diphenic[10] acids.

EXPERIMENTAL

Reagents

Thorium nitrate 4-hydrate was obtained from the Lindsay Chemical Co., West Chicago, Ill..

The organic acids were obtained from Eastman Organic Chemicals, Rochester 3, N.Y., and K & K Laboratories, Long Island City 1, N. Y.

All other reagents were of C.P. quality.

Thermobalance

The thermobalance used has been previously described[11]. The heating rate employed was 5.4° per minute.

All samples were run in duplicate.

Preparation of precipitates

The precipitates were prepared as previously described[3–10]. They were air-dried for 24 hours at room temperature before pyrolysis on the thermobalance.

DISCUSSION

The thermal decomposition curves are given in Figs. 1 and 2. Since in certain cases the composition of the initial precipitates deviated appreciably from known stoichiometries, the ThO_2 contents are presented in Table I. The minimum oxide level temperatures are also given in Table I.

Most of the precipitates reported in this investigation were basic salts. The general formula can be written as $Th(OH)_{4-n}A_n$, where n is the number of organic acid ligands,

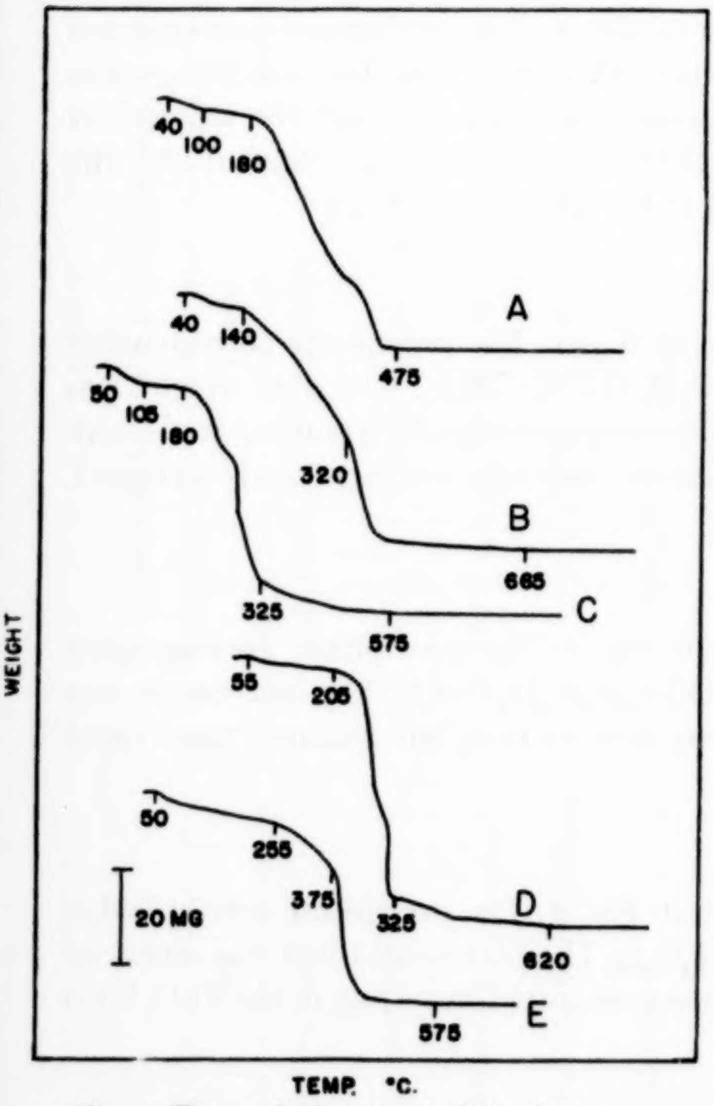

Fig. 1. Thermolysis curves of thorium precipitates.
A. Thorium phenylpropionate.
B. Thorium acetyl-*o*-salicylate.
C. Thorium phenoxyacetate.
D. Thorium 2,4,5-trichlorophenoxyacetate.
E. Thorium 2,2′-diphenate.

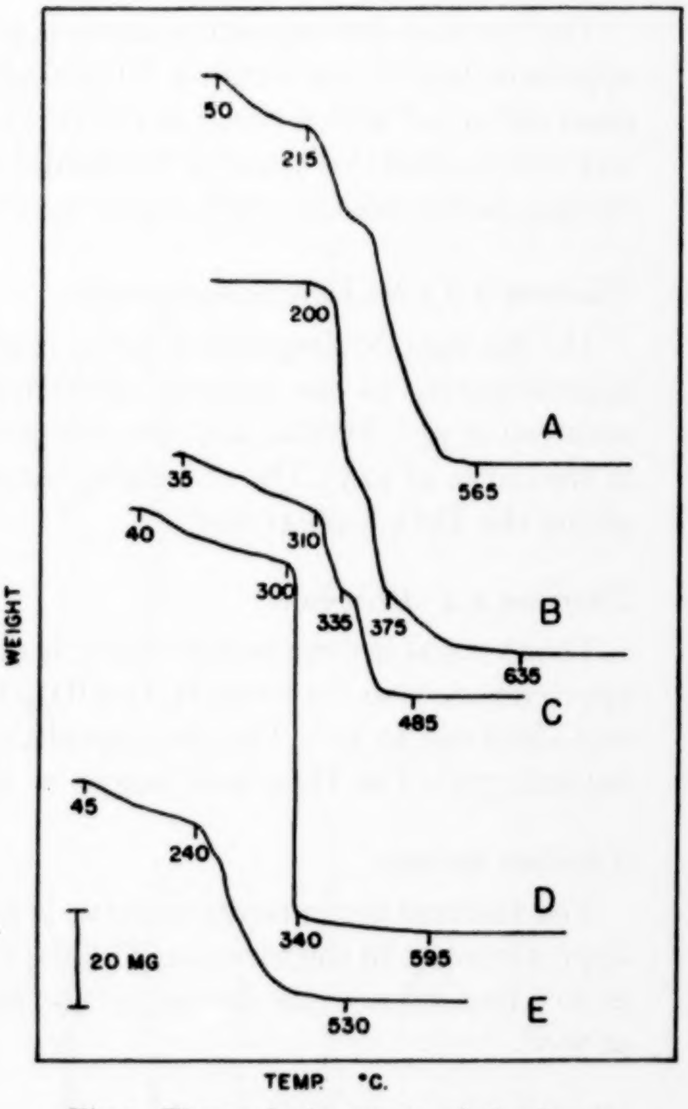

Fig. 2. Thermolysis curves of thorium precipitates.
A. Thorium tannate.
B. Thorium 5-bromosalicylate.
C. Thorium 1-hydroxy-2-naphthoate.
D. Thorium 5-nitrosalicylate.
E. Thorium phenylglycine-*o*-carboxylate.

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A^-, per thorium ion. As in the previous studies[1,2], the basic salts began to lose weight in the 40 to 50° temperature range.

Thorium phenylpropionate

The thermal decomposition curve is given in Fig. 1. The precipitate corresponded approximately to the formula, $Th(OH)_2(C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}COO)_2$. The first weight loss was observed at 40°. Beyond 180° the decomposition became quite rapid, resulting in the ThO_2 level at 475°.

Thorium acetyl-o-salicylate

The thermal decomposition curve is given in Fig. 1. The precipitate corresponded to the formula, $Th(OH)_2(CH_3{\cdot}CO_2{\cdot}C_6H_4{\cdot}COO)_2$. The compound began to lose weight at 40°. Beyond 140° the decomposition became quite rapid, resulting in the ThO_2 level at 665°.

Thorium phenoxyacetate

The thermal decomposition curve is given in Fig. 1. The precipitate corresponded approximately to the formula, $Th(OH)_2(C_6H_5{\cdot}O{\cdot}CH_2{\cdot}COO)_2$. The first weight loss was observed at 50° with a break in the curve appearing at 105°. Although the weight loss was slow beyond this point, a horizontal weight level was not found. Beyond 180° the decomposition became quite rapid, resulting in the ThO_2 level at 575°.

Thorium 2,4,5-trichlorophenoxyacetate

The thermal decomposition curve is given in Fig. 1. The precipitate corresponded approximately to the formula, $Th(OH)(Cl_3C_6H_2{\cdot}O{\cdot}CH_2{\cdot}COO)_3$. The first weight loss occurred at 55°. Beyond 205° the compound decomposed rapidly, resulting in a break in the curve at 325°. The remaining carbonaceous material was then slowly oxidized, giving the ThO_2 level at 620°.

Thorium 2,2'-diphenate

The thermal decomposition curve is given in Fig. 1. The precipitate corresponded approximately to the formula, $Th(OH)_3(HOOC{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}COO)$. The first weight loss was observed at 50°. The decomposition was slow at first but became more rapid beyond 375°. The ThO_2 level began at 575°.

Thorium tannate

The thermal decomposition curve is given in Fig. 1. The precipitate corresponded approximately to the formula, $Th(OH)(C_{14}H_9O_9)_3$. The first weight loss was observed at 50°. Beyond 215° the decomposition became quite rapid, resulting in the ThO_2 level at 565°.

Thorium 5-bromosalicylate

The thermal decomposition curve is given in Fig. 2. The precipitate corresponded approximately to the formula, $Th(HOC_6H_3Br{\cdot}COO)_4$. This was the only compound found in this study that corresponded to the normal salt. Consequently, since normal salts are generally more stable than basic salts[2], the first weight loss was observed at

TABLE I

COMPOSITION DATA FOR THORIUM PRECIPITATES

Name	*Formula*	*% ThO_2* *Found*	*Calc.*	*Minimum oxide level temperature, °C*
Thorium phenylpropionate	$Th(OH)_2(C_6H_5 \cdot CH_2 \cdot CH_2 \cdot COO)_2$	52.2 52.3	46.79	475
Thorium acetyl-*o*-salicylate	$Th(OH)_2(CH_3 \cdot COO \cdot C_6H_4 \cdot COO)_2$	42.6 42.4	42.30	665
Thorium phenoxyacetate	$Th(OH)_2(C_6H_5 \cdot O \cdot CH_2 \cdot COO)_2$	48.6 48.6	46.47	575
Thorium 2,4,5-trichlorophenoxyacetate	$Th(OH)(Cl_3C_6H_2 \cdot O \cdot CH_2 \cdot COO)_3$	30.4 30.4	26.09	620
Thorium 2,2′-diphenate	$Th(OH)_3(HOOC \cdot C_6H_4 \cdot C_6H_4 \cdot COO)$	56.9 56.8	50.37	575
Thorium tannate	$Th(OH)(C_{14}H_9O_9)_3$	19.3 19.6	21.72	565
Thorium 5-bromosalicylate	$Th(HOC_6H_3Br \cdot COO)_4$	25.8 25.6	24.09	635
Thorium 1-hydroxy-2-naphthoate	$Th(OH)_2(HOC_{10}H_6 \cdot COO)_2$	50.3 50.0	56.92	485
Thorium 5-nitrosalicylate		15.3 17.8		595
Thorium phenylglycine-*o*-carboxylate	$Th(OH)_3(HOOC \cdot CH_2 \cdot NH \cdot C_6H_4 \cdot COO)$	55.0 55.1	55.34	530

a higher temperature, 200°. Beyond this temperature however, the compound decomposed rapidly, giving the ThO_2 level at 635°.

Thorium 1-hydroxy-2-naphthoate

The thermal decomposition curve is given in Fig. 2. The precipitate corresponded roughly to the formula, $Th(OH)_2(HOC_{10}H_6 \cdot COO)_2$. This compound was the least stable of all of the precipitates investigated in this study. The first weight loss occurred at 35°. Beyond 310° the decomposition became quite rapid, giving a break in the curve at 335°, then the ThO_2 level 485°.

Thorium 5-nitrosalicylate

The thermal decomposition curve is given in Fig. 2. It was impossible to calculate the composition of the precipitate by determining the ThO_2 content on ignition in the thermobalance. This was due to the almost explosive decomposition of the compound at 300°. Because of this rapid decomposition, some of the decomposing material could have been easily ejected from the thermobalance pan, thus giving a low ThO_2 content. The precipitate began to lose weight at 40°. The weight loss was gradual at first but became extremely rapid beyond 300°. The ThO_2 level began at 595°.

Thorium phenylglycine-o-carboxylate

The thermal decomposition curve is given in Fig. 2. The precipitate corresponded to formula, $Th(OH)_3(HOOC \cdot CH_2 \cdot NH \cdot C_6H_4 \cdot COO)$. The first weight loss was observed at 45°. Beyond 240° the decomposition became quite rapid, resulting in the ThO_2 level at 530°.

SUMMARY

The thermal decomposition of the thorium salts of tannic (digallic), 5-bromosalicylic, 5-nitrosalicylic, 1-hydroxy-2-naphthoic, phenylglycine-*o*-carboxylic, phenylpropionic, acetyl-*o*-salicylic, phenoxyacetic, 2,4,5-trichlorophenoxyacetic and 2,2'-diphenic acids was investigated on the thermobalance. Most of the precipitated compounds were of a basic composition, corresponding to the general formula, $Th(OH)_{4-n}(A)_n$, where A^- is the organic acid ligand. The first weight losses were found from 35 to 200° with minimum oxide level temperatures occurring in the 475 to 665° temperature range.

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SEPARATION OF ZINC AND COPPER WITH CYANOACETAMIDE IN THE DETERMINATION OF ZINC

by

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INTRODUCTION

One of the most important problems concerned with the spectrophotometric determination of zinc is the interference by copper. The two metals are so similar in chemical nature that it is extremely difficult to separate microgram quantities of one element from the other without utilizing extraction techniques. Complexing agents which will mask copper usually mask zinc also.

A direct spectrophotometric procedure for determining zinc in the presence of copper should utilize a colorimetric reagent not reactive to copper or either a reagent which will selectively mask or complex the copper, or a separation technique involving the extraction of either element. The dithizone[1] and dithiocarbamate[2] separations are examples of the latter. It is also possible to separate copper from zinc using ion-exchange chromatography[3].

Recently, an indirect method for the determination of small amounts of zinc has been proposed[4]. This procedure consists of determining both zinc and copper, then copper alone, to obtain the zinc value by difference.

This investigation reveals the new use of cyanoacetamide ($CNCH_2CONH_2$) for the elimination of copper interference in the zinc determination with "zincon"[5] (for 2-carboxy-2′-hydroxy-5′-sulfoformazylbenzene).

EXPERIMENTAL

Known amounts of copper and/or zinc were placed in 50 ml pyrex beakers. To this was added 10 ml of deionized water followed by 10 ml of a Clark and Lubs buffer, pH 9.4[6]. The pH of the resulting solutions was checked with a Beckman model N-1 pH meter. With the copper and zinc standards, no pH adjustment was necessary. Then 40 mg of cyanoacetamide was placed in the beaker, the solutions mixed thoroughly and transferred to 50 ml pyrex volumetric flasks. To each flask 1 ml of "zincon" reagent (0.130 g zincon dissolved in 2 ml 1*N* NaOH, diluted to 100 ml with deionized water) was added, the contents were mixed, diluted to the mark with deionized water and mixed again. The color of the resulting solutions was read in a Bausch and Lomb "Spectronic-20" spectrophotometer at 620 mμ. The standard zinc curve was prepared in an identical manner. The study of other possible interfering ions followed the same procedure.

RESULTS AND DISCUSSION

In Table I, the effectiveness of cyanoacetamide in eliminating the interference of copper is shown. At all combinations of zinc and copper concentrations, cyanoacetamide was satisfactory in promoting the accurate determination of zinc in the presence of copper.

The effectiveness of adding cyanoacetamide solutions to the zinc and copper stand-

TABLE I

DETERMINATION OF MICROGRAM AMOUNTS OF ZINC IN THE PRESENCE OF COPPER

Copper present (γ)	*Zinc present* (γ)	*Zinc found* (γ)
100.0	50.0	49.7
0.0	50.0	49.7
50.0	40.0	39.0
0.0	40.0	39.0
10.0	30.0	30.4
10.0	30.0	31.0
30.0	30.0	29.0
50.0	30.0	28.5
70.0	30.0	28.0
100.0	30.0	30.0
0.0	30.0	29.8
30.0	20.0	19.0
0.0	20.0	19.0
10.0	10.0	10.0
30.0	10.0	9.6
50.0	10.0	11.0
0.0	10.0	9.6
30.0	0.0	0.0

TABLE II

THE EFFECT OF VARYING AMOUNTS OF CYANOACETAMIDE ON THE DETERMINATION OF ZINC

Amount cyanoacetamide added (*mg*)	*Zinc present* (γ)	*Zinc found* (γ)
30.0	30.0	30.5
40.0	30.0	29.8
50.0	30.0	29.5

TABLE III

EFFECT OF OTHER IONS ON THE DETERMINATION OF ZINC WITH CYANOACETAMIDE AND ZINCON

Ion present (γ)		*Zinc present* (γ)	*Zinc found* (γ)
Co^{+2}	5.0	40.0	40.5
Fe^{+3}	30.0	40.0	29.0
Fe^{+3}	50.0	40.0	25.0
Fe^{+3}	100.0	30.0	15.0
Mn^{+2}	100.0	30.0	0.0

ards was very poor. It appears that this compound undergoes a structural change when in solution for a number of hours and it is therefore recommended that the reagent be added in the solid form. It is possible that hydrolysis is responsible for altering the copper-masking properties of the reagent.

The color of the zinc-zincon complex under the conditions described is stable for at least 30 minutes. Absorption spectra of the zinc-zincon complex in the presence

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of cyanoacetamide was not changed from that of the zinc-zincon complex alone. Both spectra show an absorption maximum at 620 mμ.

The amount of cyanoacetamide added within prescribed limits is not critical (Table II). Following the addition of the cyanoacetamide, the color should be developed immediately.

An investigation of other possible interferences which may be alleviated by this new masking agent showed that iron and manganese seriously impair the formation or stability of the zinc-zincon complex. Cyanoacetamide did not eliminate the iron and manganese interference (Table III). A further detailed study of foreign ion interference was not undertaken as it appears that the same interferences are in evidence as mentioned previously[5].

ACKNOWLEDGEMENT

The generosity of Kay-Fries Chemicals, Inc., New York, N.Y. in supplying the experimental quantity of cyanoacetamide is greatly appreciated.

SUMMARY

The new use of cyanoacetamide as a selective masking agent for copper in the determination of microgram amounts of zinc with zincon is described. It is very possible that the unique masking action of this compound may have importance in eliminating the interference of copper in other spectrophotometric and titrimetric procedures for zinc thereby reducing the time required to complete the analysis by decreasing or eliminating laborious separation or extraction techniques. The possibility of using cyanoacetamide as a masking agent for other ions should not be overlooked.

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CHELATE FORMATION OF AMMONIUM AURINTRICARBOXYLATE WITH BIVALENT COPPER

PART I. PHYSICO-CHEMICAL INVESTIGATION OF THE COMPOSITION, STRUCTURE AND STABILITY

by

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HAMMET AND SOTTERY[1] reported in 1925 that ammonium aurintricarboxylate forms a red coloured lake with aluminium salts, and the reagent was subsequently applied to the determination of aluminium. On account of its applications in aluminium analysis, the reagent came to be known as Aluminon (usually abbreviated as AN). MIDDLETON[2] studied the reaction of Aluminon with the hydroxides of beryllium, rare earth metals, zirconium and thorium, while COREY AND ROGERS[3] studied colour formation with scandium, gallium, indium and germanium.

It was later realized that the method of preparation of the reagent is of importance. SMITH and co-workers[4,5] emphasized the quality of the reagent and they discussed the spectral characteristics of Aluminon. They recommended that, in the preparation of the reagent, the methylene salicylic acid employed should have an average molecular weight of 300 and a melting point of 247°C. They also found that in order to obtain a stable colour, the addition of alkali should be avoided. MUKHERJI AND DEY[6], found from electrical conductance studies that the reagent behaved as a colloidal electrolyte, and they suggested that physico-chemical measurements should preferably be carried out in extremely dilute solutions.

In a recent paper, MUKHERJI AND DEY[7] noted the colour reactions of various metals with Aluminon and reported that the reagent forms coloured chelates with various metal ions including bivalent copper. Hence, a detailed investigation of the coloured metal chelates with ammonium aurintricarboxylate has been undertaken and this paper records our results with copper-Aluminon chelate. In Part II of this series, we shall present our experiments on the application of the colour formation to the determination of cupric ion on a micro-scale.

EXPERIMENTAL

Standard solutions of cupric sulphate (BDH AnalaR), and of ammonium aurintricarboxylate (BDH indicator) were prepared in doubly distilled water. A stock solution of cupric sulphate was first prepared, which was subsequently diluted as required for different sets of experiment. Aluminon solutions were prepared fresh each time before use. For measuring optical density, a Unicam SP 500 Spectrophotometer was employed, and the measurements were done in an air-conditioned room in which a constant temperature of 25°C was maintained. The individual solutions were kept immersed in a thermostat at a temperature of 25° ± 0.01°C, and the mixtures were kept at least for 15 min to attain equilibrium. For measurements 1-cm glass cells supplied with the instrument were used.

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For the measurement of electrical conductivity an L & N Kohlrausch Slidewire with an audio-frequency oscillator was employed. The conductivity cell used was of the dip type, having a cell constant of 0.132. The solutions and the mixtures were kept in an electrically operated T & M Precision Thermostat that maintained a temperature of 32° ± 0.01°C before and during measurements. The total volume was kept at 50 ml in every case.

Nature of complexes formed

Mixtures containing varying proportions of cupric sulphate: Aluminon were prepared, and the optical densities of the mixtures were measured at different wavelengths. The results are recorded in Tables I and II.

TABLE I

COMPOSITIONS OF THE MIXTURES

(Concentration of copper sulphate = 0.0002M)

Mixture	*Ratio* $CuSO_4$ *: Aluminon*
A	1 : 1
B	1 : 2
C	1 : 3
D	1 : 4

TABLE II

OPTICAL DENSITIES OF THE MIXTURES AT DIFFERENT WAVELENGTHS

Wavelength mμ	*Optical density*			
	A	*B*	*C*	*D*
430	0.060	0.070	0.065	0.065
440	0.075	0.080	0.085	0.085
450	0.095	0.110	0.110	0.110
460	0.105	0.120	0.135	0.130
470	0.115	0.130	0.140	0.145
480	0.115	0.140	0.150	0.155
490	0.125	0.150	0.160	0.175
500	0.135	0.165	0.175	0.190
510	0.165	0.200	0.210	0.210
520	0.195	0.220	0.250	0.240
530	0.205	0.240	0.265	0.275
540	0.210	0.245	0.265	0.265
550	0.170	0.220	0.250	0.240
560	0.145	0.175	0.195	0.195
570	0.100	0.125	0.140	0.140
580	0.050	0.070	0.080	0.090
590	0.020	0.040	0.050	0.045
600	0.005	0.020	0.025	0.015
625	0.005	0.000	0.001	0.000

The observations indicate that maximum absorption occurs in all the mixtures at a spectral region of 540 mμ. This shows that only one complex is formed in solution.

Stoichiometry of the components

The composition of the complex was determined by using JOB's method of continuous variation[8]. The total volume in each case was 50 ml. The optical densities were measured at 540 and 440 mμ. It may be mentioned that at the dilutions and wavelengths used, copper sulphate solutions have no absorption. The results of the spectrophotometric studies are represented graphically in Fig. 1-4, while those obtained by conductance studies are shown in Fig. 5. In the figures, *c* represents the concentration of cupric sulphate, while *p* the ratio c'/c, c' being the concentration of the chelating agent.

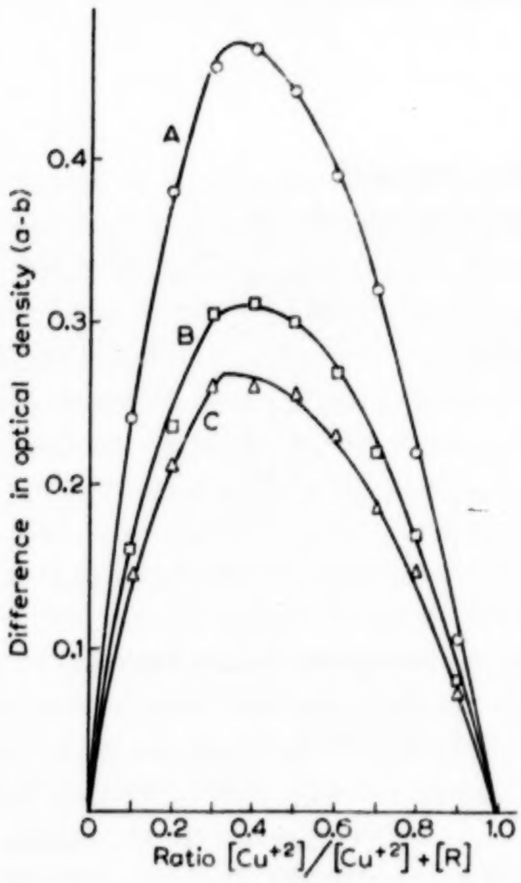

Fig. 1.

λ = 540 mμ
A, $c = 2.0 \times 10^{-4}M$
$p = 1$
B, $c = 1.2 \times 10^{-4}M$
$p = 1$
C, $c = 1.0 \times 10^{-4}M$
$p = 1$

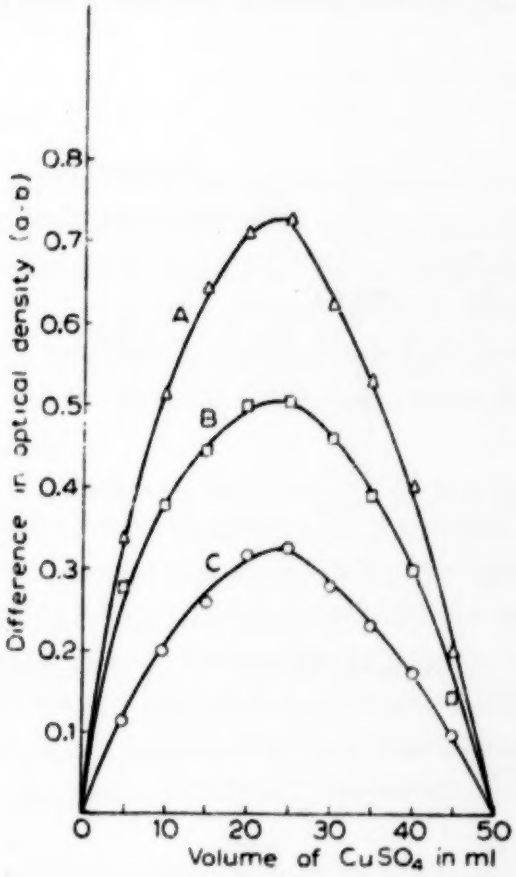

Fig. 2.

λ = 540 mμ
A, $c = 2.0 \times 10^{-4}M$
$p = 2$
B, $c = 1.2 \times 10^{-4}M$
$p = 2$
C, $c = 1.0 \times 10^{-4}M$
$p = 2$

RESULTS AND DISCUSSION

It may be seen from the figures that in every case the peak of the curves occurs at a ratio of 1:2 of the reactants, showing that the composition of the chelate is 1:2. It has been found that on mixing solutions of cupric sulphate and Aluminon, there is an appreciable increase in acidity of the mixture. This shows that hydrogen ions

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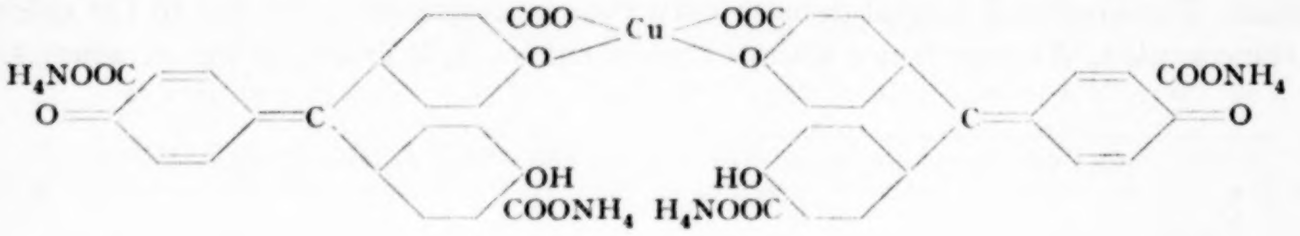
are liberated as a result of the chelation process. It appears, therefore, that chelation occurs between the carboxylic oxygen and the adjacent phenolic oxygen. This also indicates that the quinoid oxygen remains free. The structure of the chelate is probably as follows:



We have employed the optical density data to elucidate the composition of complexes and have followed a slightly modified method to calculate the formation constant. The method of continuous variation is used, and optical densities of mixtures of different compositions are measured at a fixed wavelength. The variation of optical density against $[M]/[M] + [R]$, ($[M]$ = concentration of metal ion, $[R]$ = concentration of chelating agent) is plotted graphically. In Fig. 6 such a graph is shown for the system investigated. In our case the metal ion is colourless (at the concentration and wavelength used), while the chelating agent is coloured. Hence, $[R]$ decreases with the pro-

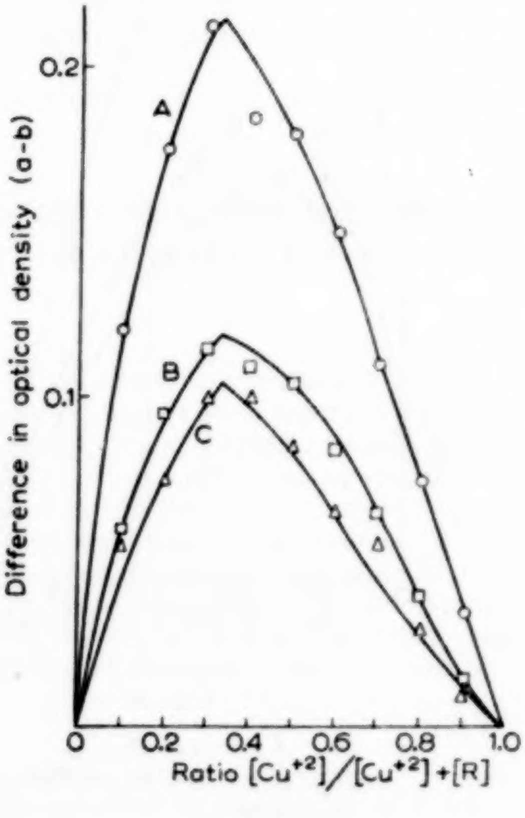


Fig. 3.

$\lambda = 440$ mμ
A, $c = 2.0 \times 10^{-4} M$
$p = 1$
B, $c = 1.2 \times 10^{-4} M$
$p = 1$
C, $c = 1.0 \times 10^{-4} M$
$p = 1$

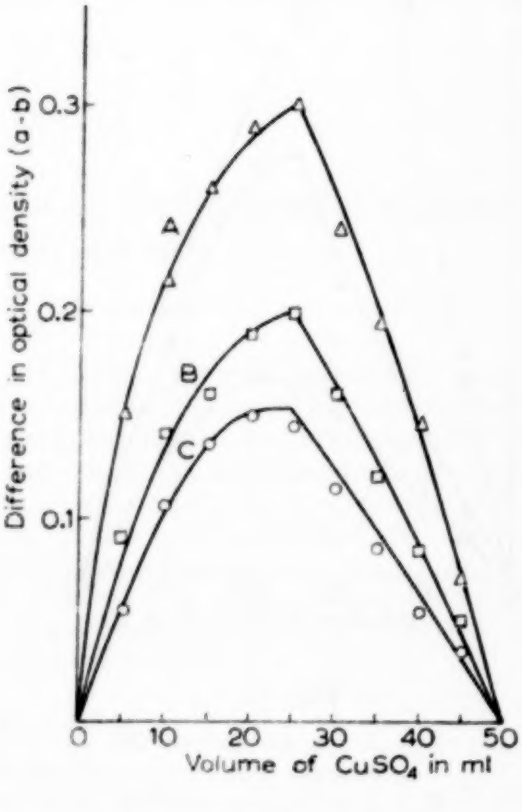


Fig. 4.

$\lambda = 440$ mμ
A, $c = 2.0 \times 10^{-4} M$
$p = 2$
B, $c = 1.2 \times 10^{-4} M$
$p = 2$
C, $c = 1.0 \times 10^{-4} M$
$p = 2$

gressive addition of metal ions and it may be assumed that in the descending portion of the curves, where the metal ion is in large excess, most of the chelating agent is bound up in the complex. Therefore, in this portion of the curve, optical density of the free chelating agent does not contribute substantially to the optical density of the system. The observed optical density may thus be regarded to be due to the colour of the complex. We may hence assume that in curves A, B and C, in Fig. 6, where the optical densities are the same, say 0.3, the respective amounts of the complex formed are identical.

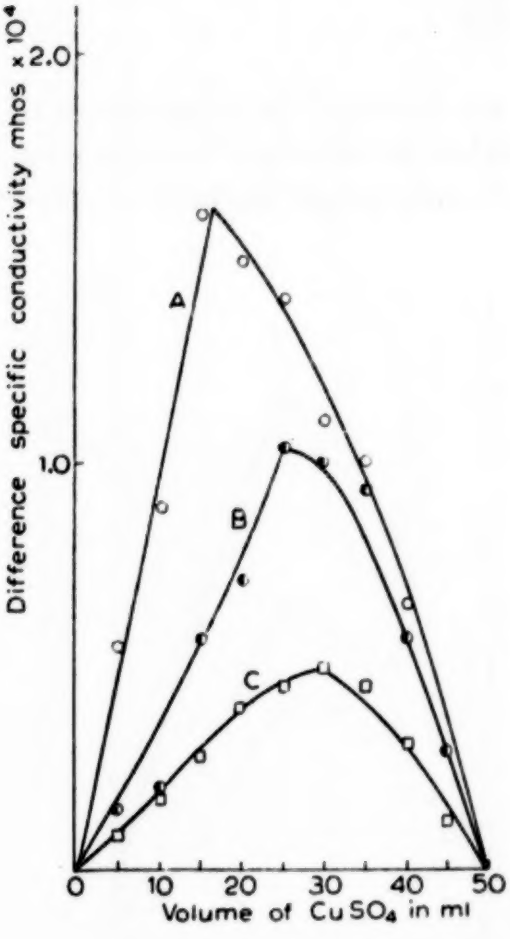


Fig. 5.

A, $c = 2.0 \times 10^{-3} M$
$p = 1$
B, $c = 1.0 \times 10^{-3} M$
$p = 2$
C, $c = 0.5 \times 10^{-3} M$
$p = 2$

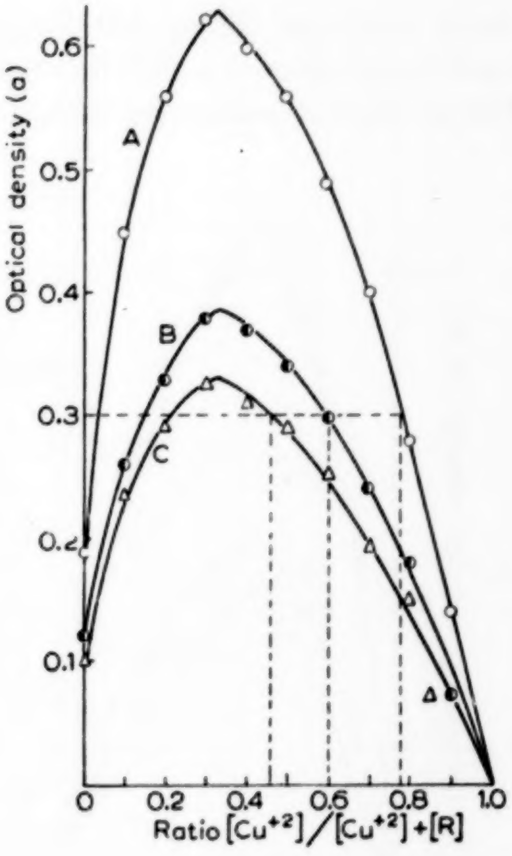


Fig. 6.

$\lambda = 540$ mμ
A, $c = 2.0 \times 10^{-4} M$
$p = 1$
B, $c = 1.25 \times 10^{-4} M$
$p = 1$
C, $c = 1.0 \times 10^{-4} M$
$p = 1$

In this system the ratio of the reactants is 1:2:

$$A + 2\,B = AB_2$$

The formation constant

$$K = \frac{x}{(a-x)\,(b-2x)^2} \quad \ldots\ldots\ldots\ldots \quad (1)$$

where x = concentration of the complex at equilibrium, and a and b are the initial concentrations of the metal ion and chelating agent, respectively. Taking two concentrations with the same optical density, *i.e.*, the same value of x, we have,

$$K = \frac{x}{(a-x)(b-2x)^2} = \frac{x}{(a'-x)(b'-2x)^2} \quad \text{(2)}$$

$$\text{or } x^2\left[4\left\{(a+b)-(a'+b')\right\}\right] + x\left[b'^2-b^2+4(a'b'-ab)\right] + ab^2 - a'b'^2 = 0$$

$$\therefore x = \frac{-\left[b'^2-b^2+4(a'b'-ab)\right] \pm \sqrt{\left[b'^2-b^2+4(a'b'-ab)\right]^2 - 4\left[4\left\{(a+b)-(a'+b')\right\}(ab^2-a'b'^2)\right]}}{8\left[(a+b)-(a'+b')\right]} \quad \text{(3)}$$

Thus, from a knowledge of two initial concentrations of a and b, the value of x can be calculated from eqn. (3) By substituting the value of x in eqn. (1), K can be found.

We have calculated the formation constant of cupric-ammonium aurintricarboxylate chelate by the above method and our value comes to be $6.45 \cdot 10^8$ at 25°C.

The dissociation constant has been calculated, and also the free energy of formation, with the help of the relation:

$$\triangle F = RT \log K_d \quad \text{(4)}$$

The terms have their usual significance, and K_d is the dissociation constant. The free energy of formation at 25°C works out to be —14.6 kcal.

SUMMARY

The formation of a coloured chelate, having λ_{max} at 540 mμ, between cupric ions and ammonium aurintricarboxylate has been reported. It has been concluded that only one complex having metal: reagent ratio of 1:2 is formed in solution. The method adopted for investigation has been the continuous variation method, using spectrophotometric and electrical conductance measurements. It has been observed that there is an increase in acidity on mixing the reactants, which shows that hydrogen ions are liberated as a result of chelation. It has been suggested that chelation occurs between the phenolic oxygen and the adjacent carboxylic oxygen.

A method has been presented for the calculation of formation constant from spectrophotometric data and the value of K in the case of the chelate investigated has been calculated to be $6.45 \cdot 10^8$. The free energy of formation works out to be —14.6 kcal at 25°C.

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A PRELIMINARY STUDY OF A COLORIMETRIC METHOD FOR ANISOLE DETERMINATION

by

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INTRODUCTION

A well-known colour reaction of aromatic compounds is that with formalin solution and concentrated sulphuric acid. LEROSEN, MORAVEK AND CARLTON[1] quote it for chromatographic work and FEIGL[2] gives an extensive list of aromatic compounds showing the test, using the same reagent quantities as LEROSEN and co-workers, namely, 0.2 ml of 37% formalin solution and 10 ml of concentrated sulphuric acid.

As a basis for quantitative analysis, the reaction has been little used. It serves for approximate analysis of benzene and other lower aromatic hydrocarbons[3]. MORRIS, STILES AND LANE[4] have used it to determine small amounts of these hydrocarbons in water by extraction with carbon tetrachloride (25 ml) and development of colour with 5 ml of a mixture prepared from 1 ml of 37% formalin + 100 ml concentrated sulphuric acid.

It was considered of interest to examine more fully the possibility of using the colour reaction as a basis for the analysis of:

(i) Aromatic compounds in the presence of non-aromatic.

(ii) One aromatic compound, reacting more sensitively, in the presence of other, less reactive aromatic compounds.

Anisole, a compound otherwise difficult to analyse in microquantities, was chosen for the initial work.

EXPERIMENTAL

The reaction conditions or factors to be examined are:

(1) A solvent to dissolve all reactants.
(2) Concentration of sulphuric acid.
(3) Reaction temperature.
(4) Time of colour development.
(5) Concentration of formaldehyde.
(6) Concentration of water.
(7) Concentration of anisole.

In the present work, glacial acetic acid was selected as solvent and, after preliminary study, the sulphuric acid concentration was fixed at 10% v/v and the reaction temperature at 50°.

Reagents

Sulphuric acid/acetic acid. 50 ml of concentrated sulphuric acid (96% by weight) were added gradually to about 150 ml of glacial acetic acid, with cooling so as to avoid a rise in temperature to more than about 40°. This was then diluted to 250 ml with further acetic acid, and the mixture left several days before use.

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2% formaldehyde solution. 2 ml of 35% formalin solution were diluted to 100 ml with glacial acetic acid. This stock solution was diluted by a factor of 10 or 20 with acetic acid as required.

Anisole solution. 2.2 g of distilled anisole were diluted to 100 ml with acetic acid. This stock solution was diluted by a factor of 10 or 50 with acetic acid, as required.

The reaction mixture was prepared from 2.5 ml of the sulphuric acid/acetic acid reagent + formaldehyde solution + anisole solution, and the total volume made up to 5 ml with acetic acid.

Procedure

The freshly made-up reaction mixture was placed in a thermostatically controlled bath at 50°, and the time of colour development was measured from the moment of introduction. The light absorption was measured on the warm solution in test tubes of 14 mm cross-section, using the Lumetron colorimeter, filter 490 mμ. All readings are optical densities with the instrument set to zero with no tube in the holder.

RESULTS

(a) Time of colour development

As seen from some examples given in Table I, the colour intensity increases rapidly during the first 15-30 min, but undergoes little change from about 45 min up to 120 min. Accordingly, an interval of 60 min was taken for subsequent quantitative work; a possible error of 1 or 2 min then introduces negligible error.

TABLE I

mg formaldehyde	*mg anisole*	*Time of colour development in min*						
		0	*15*	*30*	*45*	*60*	*90*	*120*
1.75	2.20		1.71	2.54	3.06	3.19	3.31	3.28
7.0	2.20	0.51	2.25	3.14	3.52	3.77	3.92	3.92
35.0	2.20		1.25	1.40	1.43	1.43	1.40	1.28
1.75	0.44	0.43	0.76	1.02	1.13	1.25	1.28	1.32
7.0	0.44		1.02	1.13	1.25	1.25	1.31	1.29
35.0	0.44		0.51	0.51	0.54	0.53	0.55	0.57

(b) Effect of formaldehyde and anisole concentrations

The effect of variation of formaldehyde concentration for different amounts of anisole is shown in Fig. 1. All curves pass through a rather attenuated maximum. The optimum quantity of formaldehyde for colour development rises in proportion to the amount of anisole, and under the reaction conditions used here, the ratio of formaldehyde: anisole is about 2:1. This represents a much higher ratio than that required by the probable initial reaction of

$$2\,\mathrm{Ar.H} + \mathrm{H\,CHO} \rightarrow \mathrm{Ar.CH_2.Ar} + \mathrm{H_2O}$$

postulated by FEIGL[2], according to which the ratio formaldehyde: anisole would be 30:216, *i.e.*, about 1:7.

After consideration of the curves in Fig. 1, it was decided that the most suitable fixed amount of formaldehyde for trial in a quantitative determination of anisole, was 7 mg., *i.e.*, 1 ml of the 2% formaldehyde reagent. Curve A in Fig. 2, based on the use of this amount, shows the relation of optical density to the amount of anisole. It is improbable that curve A would be a straight line, since the depressive effect of excess

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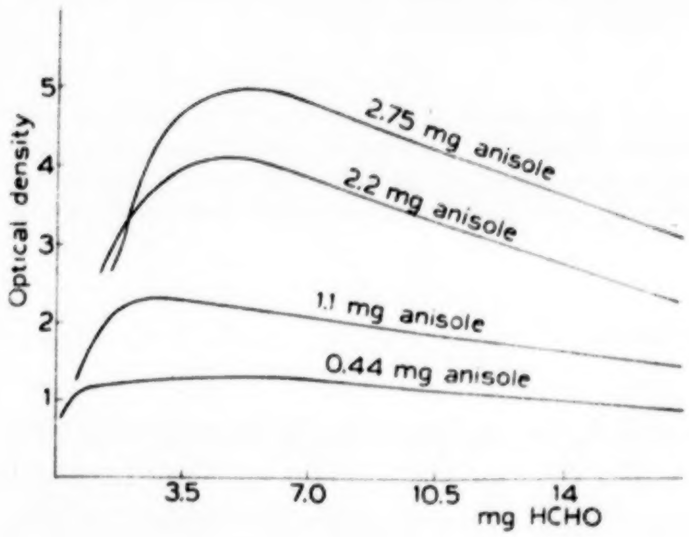

Fig. 1.
Effect of anisole and formaldehyde on colour development
(5 ml of reaction mixture).

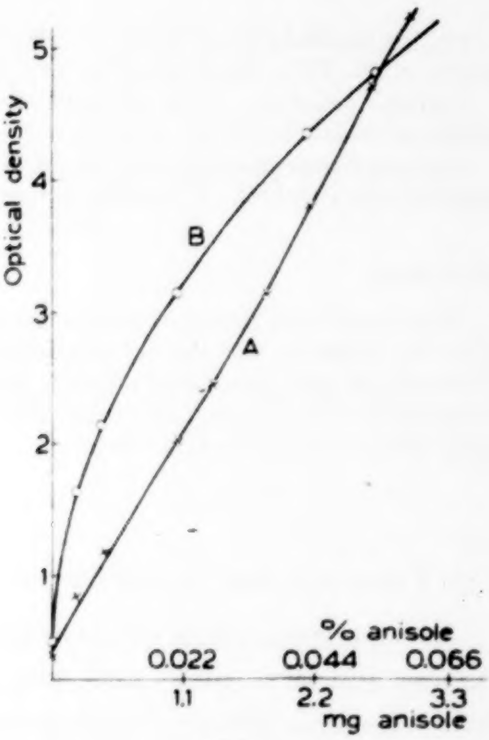

Fig. 2.
Relation of light absorption and amount of anisole
(5 ml of reaction mixture).
A, no benzene; B, in presence of 0.2 ml benzene.

formaldehyde reagent varies with the amount of anisole, and, further, the applicability of Beer's law is uncertain.

(c) Effect of water in the reaction mixture

This is shown in Fig. 3 for two anisole amounts. Acetic anhydride was used to remove water. Comparison of Fig. 1 and 3 shows that the water in the formaldehyde reagent (prepared from aqueous formalin) accounts partly, but not wholly, for the fall in colour intensity at higher concentrations of formaldehyde.

The fairly large influence of water shows the importance of protecting the hygroscopic sulphuric acid/acetic acid reagent against moisture. In the preliminary work described here, no special precautions were taken, which probably accounts for drifts sometimes observed in the results.

The reaction mixtures used contain about 0.08-0.09 ml water, made up from:

2.5 ml of 20% sulphuric acid reagent, equivalent to 0.5 ml of the 96% sulphuric acid, which thus contains 0.02 ml of water.

1.0 ml of formaldehyde reagent, equivalent to 0.02 ml of original aqueous formalin solution.

4.5 ml of about 99% acetic acid, which thus contains about 0.045 ml of water.

Total water = 0.02 + 0.02 + 0.045 = 0.085.

The sharp break in the curves of Fig. 3 thus seems to correspond to the removal of the last traces of water, after which acetic anhydride in excess evidently markedly depresses the colour development.

In the second part of the work, the colour development of anisole/benzene mixtures was studied, with a view to eventual analysis of small quantities of anisole in benzene.

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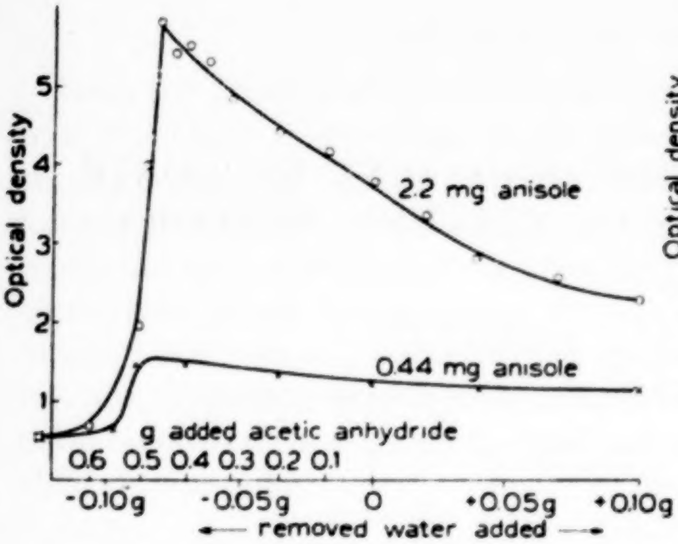

Fig. 3.
Effect of water on colour development (5 ml of reaction mixture).

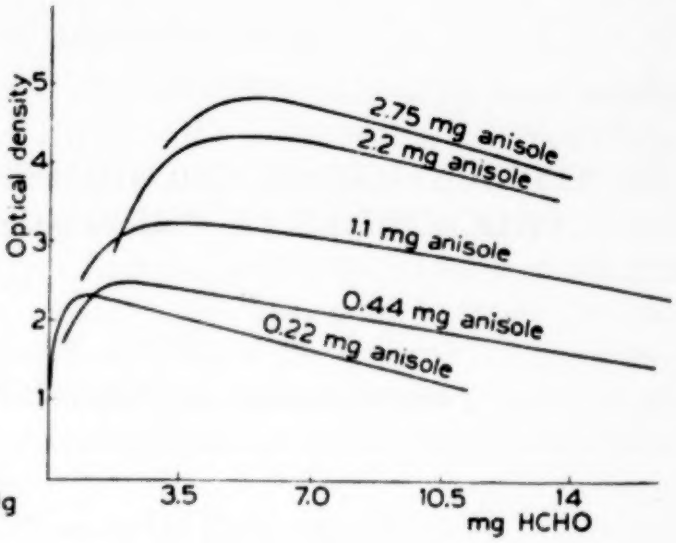

Fig. 4.
Effect of anisole and formaldehyde on colour development in presence of 0.2 ml of benzene (5 ml of reaction mixture).

The same reagents and procedure were used as above, except that the reaction mixtures contained 0.2 ml of benzene. In blank determinations without anisole this amount of benzene was found to give negligible colour development.

The effect of variation of formaldehyde concentration for different amounts of anisole is shown in Fig. 4. Maxima appear as in Fig. 1: the most noteworthy feature is that although the benzene alone produces sensibly no colour, it influences the colour development due to the anisole, especially at low anisole concentrations.

Curve B in Fig. 2 shows the relation of optical density and amount of anisole, using 7 mg formaldehyde (as for curve A) and in the presence of 0.2 ml of benzene. It is more rounded than curve A, but could nevertheless be used to determine small amounts of anisole in benzene (up to about 2% by weight).

This preliminary work is being developed and extended with particular emphasis on a study of the variations of sulphuric acid concentration, temperature and time of colour development, so as to find optimum conditions for a colorimetric method. This and attempts to apply a similar analysis to other aromatic compounds also difficult to determine by other methods (*e.g.* tetralin) will, it is hoped, form the subject of later publications.

SUMMARY

The colour reaction between anisole, concentrated sulphuric acid and formaldehyde has been studied in glacial acetic acid as solvent. The reaction can be used for the quantitative colorimetric analysis of anisole in mixtures with acetic acid and with benzene.

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APPLICATION OF COLORIMETRIC END-POINT TO IODATE PROCEDURES IN PRESENCE OF MERCURIC MERCURY

by

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Iodate acts as a strong oxidising agent in acid medium and its reduction proceeds either to iodide, iodine, or unipositive iodine state, depending upon the acidity conditions[1]. The quantitative reduction of iodate to iodide is difficult to attain. However, the presence of mercuric ions facilitates this reduction to form a stable complex, $[\mathrm{Hg\,I_4}]^{-2}$, at low acidity[2]. The complex is decomposed at high acidity and the liberated iodide is oxidised to iodine and then to unipositive iodine by excess of iodate added. Consequently, in the titration of a reductant such as As(III) with iodate in acid medium and in the presence of mercuric ions two end-points are possible, the first corresponding to the reduction of iodate to iodide at low acidity and the second corresponding to the conversion of iodide to the unipositive iodine stage at a comparatively high acidity. As the reduction of iodate proceeds to iodide, a red colour of iodine is gradually developed and its intensity increases to maximum half way through the titration and again falls to a minimum value as this iodine is reduced to iodide, this conversion being facilitated by the binding of iodide by Hg^{+2} ions. At high acidity, as the mercuric iodide complex is decomposed and the liberated iodide is oxidised by excess iodate, there is again a development of iodine colour, which, as in the former case, grows in intensity and subsequently falls to a minimum constant value corresponding to the iodine monochloride end-point.

The present investigation was carried out in order to utilise these observations for the spectrophotometric titrations of various reductants, such as arsenic(III), hydrazine, thiosulphate and thiocyanate, by iodate procedures. The determination of arsenic was carried out both in hydrochloric and sulphuric acid medium, while the titrations of hydrazine, thiosulphate and thiocyanate were found to be feasible only in the hydrochloric acid medium. Direct titration of thiocyanate with iodate was inconveniently slow so the indirect procedure was adopted using arsenious oxide for back-titration of the excess iodate.

Apparatus and general procedure

The titrations were carried out in a Hilger Spekker absorptiometer unit (H 760) with a blue filter having a maximum transmission in the range of 450-500 mμ. Aliquots of the iodate solution (2 to 6 ml) were taken in the liquid cell and sufficient concentrated hydrochloric acid was added to maintain the normality between 1.5 to 2.5. About 2 ml of mercuric chloride solution (saturated at room temperature) were also added. The reductant solution was introduced from a 10-ml microburette and the progress of the titration was followed with the absorptiometer. The second end-point was obtained at a comparatively high acidity which was maintained by adding sufficient hydrochloric acid at the first end-point to increase the normality from 2 to 6. Direct titrations of the iodate were thus carried out with arsenic(III), thiosulphate and hydrazine.

DETERMINATION OF ARSENIOUS OXIDE

Both the direct and the reverse titrations of arsenic(III) with iodate were feasible in hydrochloric acid medium. In the direct titration the iodine colour developed from the beginning and, approaching its maximum intensity, disappeared at the first equivalence point. The optical density, which was initially at a maximum, decreased to a minimum value halfway through the titration and reached its initial value at the first equivalence point. In the reverse titration, when iodate was added to arsenic(III) solution, there was no change in the optical density until the equivalence point was reached. When the iodate solution was added further, the optical density passed through a minimum and then attained a constant maximum value indicating the iodine monochloride end-point.

As was observed by SCHOONOVER AND FURMAN[3] in the potentiometric titrations of trivalent arsenic with iodate the concentration of the acids is important. However, the limits of acidity for the two end-points established in the present investigations differ from those established by the above workers. The first end-point was accurately reached when the overall concentration of hydrochloric acid was between 0.5*N* to 3*N*, while an acidity of 1 to 6*N* was required so that the liberated iodide could be oxidised to the unipositive iodine stage. Consequently, in contrast to the potentiometric determination of trivalent arsenic by the above workers, more HCl need not be added after the first end-point since the initial 2*N* acidity is sufficient for both the end-points. The addition of iodate may therefore be continued directly after the first end-point.

In sulphuric acid medium iodate reduction proceeds smoothly only in the absence of mercuric ions. A very low concentration of sulphuric acid (about 0.01*N*) was required for the first end-point. The second end-point was obtained with iodate if sufficient hydrochloric acid was added at the first end-point to maintain a minimum acidity of 1 to 2*N*.

The effect of the dilution of the solutions was studied, and the results indicated that about 5 mg of trivalent arsenic could be estimated with a maximum error of 2% to 3%.

The calculations were based on the following relationships:

$$IO_3^- + 6\,H^+ + 6e \rightarrow I^- + 3\,H_2O \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

For the iodine monochloride end-point,

$$2\,I^- + IO_3^- + 6\,H^+ \rightarrow 3\,I^+ + 3\,H_2O \quad \ldots\ldots\ldots\ldots \quad (2)$$

Typical sets of readings indicating the change of optical density with the amount of titrating solution are given in Table I(A) and I(B). The effect of acidity and of dilution has been pointed out in the Tables II(A), II(B) and II(C).

TITRATION OF IODATE WITH HYDRAZINE AND THIOSULPHATE

Direct titrations of iodate solution with hydrazine and thiosulphate solutions in hydrochloric acid medium and in the presence of mercuric ions were carried out. As in the former case aliquots of iodate solution were taken in the liquid cell, and the solution of the reductant was introduced from a 10-ml microburette after the addition of sufficient hydrochloric acid and saturated mercuric chloride solution. The course of change of the iodine colour and, consequently, of the optical density was similar

TABLE I

TITRATION OF IODATE WITH ARSENIOUS OXIDE

(A) *Change of optical density with the addition of arsenious oxide* *0.00540 g of iodate, 1.8N HCl, 2 ml of satd. $HgCl_2$ and 2 ml of water*		*(B)* *Change of optical density with the addition of iodate* *0.0223 g of arsenious oxide, 1.1N HCl and 3 ml of satd. $HgCl_2$*	
Amount of arsenious oxide ml (0.1N)	*Optical density*	*Amount of iodate ml (0.025M)*	*Optical density*
0	0.80	0	0.80
0.50	0.789	1.2	0.80
1.03	0.718	1.9	0.80
1.32	0.598	2.5	0.80
1.48	0.755	2.9	0.80
1.53 1st end-point	0.809	3 1st end-point	0.70
1.58	0.809		
Amount of iodate ml (0.025M)			
0.26	0.699	0.17	0.335
0.51	0.614	0.30	0.175
1.2	0.53	0.72	0.042
2.08	0.651	1.08	0.151
2.435	0.765	1.43	0.585
2.465 2nd end-point	0.773	1.47	0.635
2.50	0.773	1.52 2nd end-point	0.675
		1.57	0.675

TABLE II(A)

TITRATION OF IODATE AND ARSENIOUS OXIDE IN HCl MEDIUM AND IN PRESENCE OF $HgCl_2$: EFFECT OF CONC. OF ACID AND DILUTION OF THE REAGENTS

Expt. No.	*Amount of iodate (g)*	*Total acidity in HCl (N)*	*Amount of arsenious oxide (ml 0.1N) 1st end-point*		*Total acidity ICl end-point (N)*	*Amount of iodate (ml) 2nd end-point*	
			Reqd.	*Calc.*		*Reqd.*	*Calc.*
1	0.0107	2.0	3.01	3.00	2	1.01	1.00
2	0.01605	1.1	4.50	4.50	1.1	1.52	1.50
3	0.01873	1.5	5.28	5.25	5.2	1.76	1.75
4	0.02141	1.4	6.04	6.00	5.2	1.99	2.00
5	0.00540	1.3	1.52	1.50	1.2	1.07	1.00
6	0.00215	1.0	6.09 (10 × dil.)	6.00	2.8	0.94	1.00
7	0.00108	1.6	6.12 (20 × dil.)	6.00	1.56	0.48	0.50

to that in the case of trivalent arsenic. The reaction, however, was slow and good stirring was required after each addition of the reductant. About 10 mg of hydrazine and the same amount of thiosulphate could be detected from a 3-ml solution with a precision of 97% to 98%. The calculations were based on similar relationships. Typical titration results are given in Tables III(A) and III(B).

INDIRECT DETERMINATION OF THIOCYANATE BY IODATE–ARSENIOUS OXIDE TITRATION

Direct titration of thiocyanate with iodate was not feasible. So the indirect way of adding excess of iodate to thiocyanate and back-titrating the excess with standard

TABLE II(B)

TITRATION OF ARSENIC WITH IODATE IN HCl MEDIUM AND IN PRESENCE OF MERCURIC IONS: EFFECT OF ACIDITY AND DILUTION OF THE REAGENTS

Expt. No.	*Amount of arsenious oxide (g)*	*Total acidity in HCl (N)*	*Amount of iodate (ml 0.025M) 1st end-point*		*Acidity for ICl end-point (N)*	*Amount of iodate (ml) 2nd end-point*	
			Reqd.	*Calc.*		*Reqd.*	*Calc.*
1	0.02226	0.5	2.97	3	0.5	—	—
2	0.02226	1	2.96	3	0.88	1.45	1.50
3	0.02226	1.5	2.95	3	1.34	1.40	1.50
4	0.01484	4	2.00	2	3.4	1.05	1.00
5	0.00742	5	—	—	4.8	0.52	0.50
6	0.00297	0.92	2.03 (5t. dil.)	2	2.8	2.97	1.00
7	0.00223	1.5	1.5 (5t. dil.)	1.5	3.0	0.75	0.75
8	0.00148	1.16	1.0 (5t. dil.)	1	1.12	0.49	0.50

TABLE II(C)

TITRATION OF IODATE AND ARSENIOUS OXIDE IN SULPHURIC ACID MEDIUM AND IN THE ABSENCE OF MERCURY IONS

Expt. No.	*Amount of iodate (g)*	*Total acidity in H_2SO_4 (N)*	*Amount of arsenious oxide (ml 0.1N) 1st end-point*		*Acidity in HCl for ICl end-point (N)*	*Amount of iodate (ml 0.025M) 2nd end-point*	
			Reqd.	*Calc.*		*Reqd.*	*Calc.*
1	0.01605	0.15	4.55	4.50	—	—	—
2	0.01605	0.015	4.5	4.50	2.0	1.46	1.50
3	0.0107	0.015	3.05	3.00	1.6	0.96	1.00
4	0.0107	0.03	3.00	3.00	—	—	—
5	0.0107	0.015	3.00	3.00	2.0	1.05	1.00

TABLE III(A)

TITRATION OF IODATE WITH HYDRAZINE AND *vice versa* IN HCl MEDIUM AND IN PRESENCE OF MERCURIC IONS

Expt. No.	*Amount of iodate (g)*	*Total acidity in HCl (N)*	*Amount of hydrazine (ml 0.025M) 1st end-point*		*Acidity for ICl end-point (N)*	*Amount of iodate (ml 0.025M) 2nd end-point*	
			Reqd.	*Calc.*		*Reqd.*	*Calc.*
1	0.02141	1.5	6.03	6.00	5	2.02	2.00
2	0.02141	1.7	5.98	6.00	4	2.03	2.00
3	0.01605	1.4	4.58	4.50	4.15	1.52	1.50
4	0.01605	1.4	4.52	4.50	4.15	1.51	1.50
5	0.0107	1	3.01	3	4	1.01	1.00

arsenic solution was adopted. A difference in the oxygen equivalents taken up by thiocyanate in the oxidation by thiocyanate without and with mercury ions was pointed out. In the former case it is 3 according to the equation:

$$CNS^- + H_2O + 3\ O \rightarrow CN^- + H_2SO_4$$

In the present case this was found to be 4. This was in confirmation of the result

TABLE III(B)

TITRATION OF IODATE WITH THIOSULPHATE AND *vice versa* IN HCl MEDIUM AND IN PRESENCE OF MERCURIC IONS

Expt. No.	*Amount of iodate (g)*	*Total acidity in HCl (N)*	*Amount of thiosulphate (ml 0.012N) 1st end-point*		*Acidity for ICl end-point (N)*	*Amount of iodate (ml 0.025M) 2nd end-point*	
			Reqd.	*Calc.*		*Reqd.*	*Calc.*
1	0.01659	1.3	5.57	5.70	4.5	1.52	1.55
2	0.01338	0.8	4.59	4.55	4	1.24	1.55
3	0.01338	0.9	4.52	4.55	3.7	1.23	1.25
4	0.0107	0.8	3.65	3.67	4	1.01	1.00
5	0.0107	1.0	3.64	3.67	4	0.99	1.00

obtained by BAPAT AND SHARMA[4] in the amperometric determination of thiocyanate by iodate-arsenious oxide titration, in presence of mercuric ions.

The results indicated that:
1 g molecule of thiocyanate = 2 g molecules of arsenious oxide
= 8 g equivalents of arsenious oxide

TABLE IV

INDIRECT DETERMINATION OF THIOCYANATE

Expt. No.	*Amount of thiocyanate (ml 0.0078M)*	*Total acidity in HCl (N)*	*Amount of iodate added (ml 0.025M)*	*Amount of arsenious oxide (ml 0.1N)*		*Difference (ml)*
				Calculated value to reduce iodate	*Experimental*	
1	1	1.6	2	3	2.37	0.63
2	1	1.2	2	3	2.36	0.64
3	2	1.3	4	6	4.74	1.26
4	2	1.5	3.6	5.4	4.13	1.27

ACKNOWLEDGEMENTS

Sincere thanks of the authors are due to Prof. S. S. JOSHI AND Dr. M. R. BHIDAY for their kind interest and valuable guidance during the course of the work.

SUMMARY

In the present investigations colorimetric titrations of arsenic(III), hydrazine, thiosulphate and thiocyanate have been carried out by iodate procedures in the presence of mercuric ions. A Hilger Spekker absorptiometer unit (H 760) with a blue filter having a maximum transmission in the range of 450-500 mμ was employed for the titrations. Two end-points corresponding, respectively, to the reduction of iodate to iodide and the oxidation of the liberated iodide to iodine monochloride were obtained in HCl medium, the quantitative reduction of iodate to iodide being facilitated by the presence of mercuric ions. A study of the effect of the variation of acidity and dilution of the solution was carried out for both the end-points. As little as 5 mg of the reductants could be determined with a precision of about 97% to 98%.

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THE POLAROGRAPHIC DETERMINATION OF LEAD IN TIN-BASE ALLOYS

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INTRODUCTION

The determination of lead in tin-base bearing alloys, consisting mainly of tin, antimony, copper and lead is neither rapid nor easy when classical volumetric or gravimetric methods are employed. Owing to the limited amount of lead found in these alloys, a rather large sample must be processed; also, as a rule, lead must first be separated from the remaining constituents of the alloy. A micro-volumetric method developed in this laboratory[1] employs a relatively small sample, but nevertheless takes two hours to carry out; so does the micro-electrolytic determination of lead[2]; also, the first is limited to alloys containing at least 2% lead, while the second cannot easily be applied to alloys with a lead content smaller than 5%.

The only detailed methods for the polarographic determination of lead in alloys of this kind to be found in the literature are those of COZZI[3] and possibly YONEZAKI[4]; lead has been determined, in other alloys, in diverse ways, such as: in cyanide medium by SPALENKA[5] (bronzes and zinc alloys); in pyrophosphate medium by REYNOLDS AND ROGERS[6] (zinc, aluminium alloys and brass); in thiocyanate medium by PLETENEW *et al.*[7]; in copper alloys by MILNER[8,9] and by GANDON[10]; and in tartrate medium by HERED AND HERED[11].

It therefore seemed desirable to develop a rapid polarographic method for the determination of lead in the above-mentioned alloys, to be used whenever the accuracy obtainable by polarography is sufficient.

For that purpose, sodium hydroxide $1M$ solution was chosen as the supporting electrolyte best suited to the determination of lead in this case. In this medium, tin and antimony, after oxidation, are not reduced at the D.M.E.; most of the copper present precipitates as cupric hydroxide. The remaining Cu^{+2} is reduced at approx. —0.35 V before the plumbite ion[12]. Consequently, except in the case where the amount of copper left unprecipitated appreciably exceeds the amount of lead present, no separations are necessary prior to the polarographic determination of lead.

For that reason, this research was divided into two parts:

I. The determination of lead in alloys containing 2%-20% lead;

II. The determination of lead in alloys containing 0.4%-2% lead.

EXPERIMENTAL

The apparatus, standard solutions and reagents employed were:

1. Apparatus

A Type E Leeds Northrup Electro-Chemograph (pen recording polarograph) was used. Diffusion currents, i_d, were obtained by taking the peaks of the oscillations of the residual (by extrapolation) and the limiting currents (at — 0.90 V *vs.* S.C.E.). Damping "3" was employed throughout. A capillary with a drop time t of 3.20 seconds and m (amount of mercury passing through the capillary) of 2.325 mg per second, measured at — 0.90 V *vs.* S.C.E. in 1 *M* sodium hydroxide solution, containing 0.01% gelatin, was used. The mercury column was kept at 38.3 cm and the temperature at 25 ± 0.2°C All samples were bubbled with purified nitrogen for 5 min before the polarograms were recorded. 50 ml beakers served as polarographic cells, with an agar bridge (5% agar-agar in saturated potassium chloride) making the connection to the S.C.E.

2. Standard solutions and reagents

a. Standard lead nitrate stock solution (0.01 *M*).

Lead nitrate, dried at 100°C (3.3123 g) is dissolved in distilled water and made up to 1 litre. 0.001 *M* and 0.002 *M* lead nitrate solutions were prepared by diluting this stock solution with water.

b. Copper nitrate solution, 0.1 *M*.
c. Sodium hydroxide.
d. Sodium chloride.
e. Hydrochloric acid, conc.
f. Hydrogen peroxide, 30%
g. Copper metal.
h. Antimony metal.
i. Tin metal.
j. Gelatin, 0.5% solution, freshly prepared.
k. U.S.A. National Bureau of Standards Alloy No. 54c. This alloy is a tin-base bearing metal, containing: 86.29% tin, 7.28% antimony, 1.99% lead, 4.30% copper, 0.033% iron, 0.028% bismuth, 0.012% nickel, 0.049% arsenic and 0.02% silver.

All reagents were of analytical quality.

PART I

With a view to a systematic approach to the problem, pure lead nitrate solutions were polarographed, in concentrations ranging from 2.00 m*M* to 0.04 m*M* lead, employing a supporting electrolyte 1 *M* in sodium hydroxide, containing 2.5% of sodium chloride and 0.01% of gelatin.

Table I shows some of the results obtained.

TABLE I

DETERMINATION OF LEAD IN LEAD NITRATE SOLUTIONS

Data obtained at $E_{\text{D.M.E.}}$ = —0.90 V *vs.* S.C.E. in 1 *M* NaOH, containing 2.5% NaCl and 0.01% gelatin, at 25°C.

$C_{Pb^{+2}}$ *mM*	i_d *microamp*	i_d/C	i_d/C *average*	i_d/C *relative error %*
2.00	12.70	6.35	6.42	—1.1
1.60	10.46	6.54		+1.9
1.20	7.85	6.54		+1.9
0.80	5.15	6.44		+0.5
0.40	2.62	6.55		+2.0
0.20	1.292	6.46		+0.6
0.16	1.004	6.28		—2.2
0.12	0.750	6.25		—2.7
0.08	0.501	6.26		—2.5
0.04	0.262	6.55		+2.0

Similar experiments were next carried out with solutions containing both lead and copper. Owing to the interference of the copper, satisfactory determination of lead by this method was limited to concentrations ranging from 2.00 m*M* to 0.80 m*M* lead. Table II shows some of the results obtained.

TABLE II

DETERMINATION OF LEAD IN SOLUTIONS 0.015*M* IN Cu^{+2}

Data obtained at $E_{D.M.E.}$ = —0.90 V *vs.* S.C.E. in 1*M* NaOH, containing 2.5% NaCl and 0.01% gelatin, at 25°C.

$C_{Pb^{+2}}$ m*M*	i_d *microamp*	i_d/C	i_d/C *average*	i_d/C *relative error* %
2.00	11.40	5.70	5.66	+0.7
1.80	10.20	5.67		+0.2
1.60	9.15	5.72		+1.1
1.20	6.75	5.63		—0.5
0.80	4.46	5.58		—1.4

In an attempt to extend the useful range of this method towards lower concentrations of lead, it was found that decreasing the amount of gelatin from 0.01% to 0.002% greatly improved the shape of the copper lead waves obtained and also enhanced reproducibility[13]. With this slight change, lead may be determined in the presence of copper in concentrations ranging from 2.00 to 0.06 m*M* in lead. Table III shows some of the results obtained; these were used for the calculation of an average i_d/C value, which was employed for the evaluation of all subsequent analyses of alloy No. 54c and synthetic alloy samples.

TABLE III

DETERMINATION OF LEAD IN SOLUTIONS 0.015*M* IN Cu^{+2}

Data obtained at $E_{D.M.E.}$ = —0.90 V *vs.* S.C.E. in 1*M* NaOH, containing 2.5% NaCl and 0.002% gelatin, at 25°C.

$C_{Pb^{+2}}$ m*M*	i_d *microamp*	i_d/C	i_d/C *average*	i_d/C *relative error* %
2.00	11.10	5.55	5.60	—0.9
1.60	9.20	5.75		+2.7
1.20	6.71	5.58		—0.4
0.80	4.53	5.66		+1.1
0.40	2.24	5.60		—
0.30	1.69	5.62		+0.4
0.20	1.10	5.50		—1.8
0.10	0.570	5.70		+1.8
0.08	0.446	5.59		—0.2
0.06	0.328	5.47		—2.3

Based on the above, and tested by numerous test analyses, the following procedure is recommended for the determination of lead in tin-base white metals containing 2%–20% lead.

References p. 344

Procedure A. Determination of lead in tin-base alloys containing 2%-20% lead

About 100 mg of the alloy are weighed into a 30 ml beaker and dissolved in 2 ml of concentrated hydrochloric acid, with dropwise addition of 2 ml of hydrogen peroxide, 30%. The solution is boiled to ensure complete oxidation of the tin and destruction of excess hydrogen peroxide, transferred into a 50 ml measuring flask, 20 ml of 2*M* sodium hydroxide solution and 0.2 ml of a 0.5% gelatin solution are added and the solution made up to 50 ml with distilled water. The flask is shaken thoroughly and some of the solution poured into a dry 50 ml beaker. After deaeration, a polarogram is recorded from —0.60 V to —1.00 V *vs.* S.C.E. The current range (sensitivity) of the recorder is adjusted according to the concentration of lead in the solution: the residual current, including the copper wave, is compensated as far as possible. The diffusion current, i_d is measured at —0.90 V *vs.* S.C.E., by taking the peaks of the extrapolated copper plateau and the lead wave at —0.90 V. The percentage of lead in the sample is calculated with the aid of a previously prepared calibration curve, based on measurements performed with solutions containing lead and copper, or by use of an average i_d/C value calculated from the same.

The time required for one determination is 30 minutes approx. Table IV shows some of the results obtained in test analyses carried out on samples of NBS Alloy No. 54c ($i_d/C = 5.60$).

TABLE IV

DETERMINATION OF LEAD IN ALLOY No. 54c

Alloy No. 54c *mg*	i_d *microamp*	*Pb theoretical* %	*Pb found* %	*Absolute error* %	*Relative error* %
113.35	1.232	1.99	2.01	+0.02	+1.0
146.96	1.594	1.99	2.01	+0.02	+1.0
163.60	1.725	1.99	1.95	—0.04	—2.0
217.8	2.243	1.99	1.91	—0.08	—4.0

As no suitable standard alloys containing varying amounts of lead were available, a series of synthetic alloy samples was analyzed by the above-mentioned procedure. To that end, 100 mg samples of alloy No. 54c were dissolved as described above, the appropriate amount of standard lead nitrate solution added and the analysis continued as recommended. Table V shows some of the results obtained.

TABLE V

DETERMINATION OF LEAD IN SYNTHETIC ALLOY SAMPLES

Pb theoretical	*Pb found* %	*Absolute error* %	*Relative error* %
4.00	4.06	+0.06	+1.5
8.00	8.02	+0.02	+0.25
12.00	12.00	—	—
16.00	16.20	+0.20	+1.25
20.00	19.79	—0.21	—1.05

PART II

As indicated above, the determination of small amounts of lead by the above-mentioned procedure is hampered by the presence of relatively large amounts of copper (the copper wave precedes the lead wave). Since the analysis of alloys with a low lead content were of main interest for the purpose of this work, the following possibilities for the removal of the copper interference were explored:

1. Complexation of copper with potassium cyanide. In cyanide medium copper is not reduced at the D.M.E. This method, employed by SPALENKA[5], gives adequate results, but is unpleasant to work with and necessitates the use of a hood.

2. Reduction of copper with hydroxylamine hydrochloride and its subsequent removal by precipitation as cuprous thiocyanate. This proved unsatisfactory when applied to the samples of synthetic alloys examined.

3. Removal of part of the copper by filtration of the cupric hydroxide formed on the addition of sodium hydroxide in the course of the procedure recommended above. This greatly improved the shape of the polarographic waves obtained; however, probably due to the absorption of lead on the filter paper, (from the highly alkaline solution[14]) no reproducible results could be obtained by this method.

4. Centrifugation of the solution after precipitation of cupric hydroxide did not result in its adequate removal.

5. Electrodeposition of the copper on a mercury cathode at a controlled cathode potential of —0.60 V *vs.* S.C.E.

A series of synthetic alloy samples, containing 0.5%-2% of lead and 5% of copper, was treated as in the procedure recommended above, with the insertion of a controlled electrodeposition step before polarographing. This was carried out in a small Melaven Type mercury cell at —0.60 V *vs.* S.C.E.

Good results were obtained; the method was, however, considered impractical, requiring special apparatus (for electrolysis at controlled potential) and large amounts of mercury.

6. Removal of copper as cupric oxide. This was found to provide the final solution to the problem of copper interference. The sample of alloy was dissolved as usual and the solution made alkaline with sodium hydroxide, heated to boiling and a few drops of a copper nitrate solution were added*. Most of the copper separated as black cupric oxide and was removed by filtration through a sintered glass disc or an asbestos-filled Gooch crucible. No loss of lead could be detected in this separation.

The following procedure is, therefore, recommended for the determination of lead in tin-base white metals containing 0.4%-2% of lead.

Procedure B. Determination of lead in tin-base alloys containing 0.4%-2% *of lead*

About 500 mg of the alloy are weighed into a 100 ml beaker and dissolved in 2-3 ml of concentrated hydrochloric acid, with dropwise addition of 2-3 ml of hydrogen peroxide, 30%. 20 ml of sodium hydroxide solution 4*M* are added, the solution diluted to about 50 ml with distilled water and heated to boiling. A few drops of an approx. 0.1*M* cupric nitrate solution are added and boiling is continued until the volume of the solution is reduced to about 20 ml. (To prevent losses by splashing, the beaker should be covered with a "speedyvap" contraption.) The solution is next filtered into a 50 ml measuring flask, using an asbestos filled Gooch crucible and a bell jar arrangement.

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* At this stage, prior to the addition of cupric nitrate, the solution of the samples containing copper is generally blue: no cupric hydroxide and, on boiling, no cupric oxide are formed (especially with samples with a rather low copper content). The introduction of the cupric nitrate solution seems to have the effect of breaking down a state of supersaturation, or of floculating a polarographically active colloidal cupric hydroxide.

The beaker and crucible are repeatedly rinsed with distilled water and the washings sucked into the flask. The volume of the filtrate is made up to 50 ml with distilled water (after the addition of 0.2 ml of a 0.5% solution of gelatin), the solution is polarographed and the percentage of lead in the sample calculated as described in procedure A above.

The time required for one determination is 1 hour approx. Table VI shows some of the results of test analyses carried out on samples of synthetic alloys, prepared by dissolving 400-500 mg of tin metal, 40-50 mg of antimony metal, and 20 mg of copper metal as recommended in Procedure B and adding appropriate amounts of standard lead nitrate solution.

TABLE VI

DETERMINATION OF LEAD IN ALLOYS CONTAINING 0.4% — 2% OF LEAD

Pb theoretical %	*Pb found* %	*Absolute error* %	*Relative error* %
2.00	1.99	—0.01	—0.5
1.60	1.58	—0.02	—1.25
1.20	1.21	+0.01	+0.8
0.80	0.81	+0.01	+1.25
0.40	0.41	+0.01	+2.5

SUMMARY

A polarographic method for the determination of lead in tin-base alloys is described. For alloys containing more than 2% lead no separations are necessary; in those with a lower lead content, most of the copper present must be removed as cupric oxide. Results are exact: ± 4% of the amount of lead present.

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THE POLAROGRAPHIC DETERMINATION OF INDIUM IN ZINC-BASE ALLOYS

PART I: GENERAL INTRODUCTION. THE APPLICATION OF THE LINEAR SWEEP CATHODE RAY POLAROGRAPH

by

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INTRODUCTION

The composition of zinc alloys used for die-casting must be carefully controlled if their moulding characteristics are to be preserved and if embrittlement is to be avoided. The impurities mainly responsible for this embrittlement are lead, cadmium and tin and a British Standard specification[1] therefore fixes their upper limits at: lead 0.005%, cadmium 0.005 % and tin 0.003 %.

It has been shown, in the course of some work carried out in Canada, that the presence of traces of indium also have the effect of increasing the rate and extent of embrittlement and the present work was therefore undertaken to provide sensitive methods for determining this element in zinc and zinc alloys.

The major problem in the polarographic determination of indium is the coincident reduction of cadmium in all commonly employed base electrolytes. If the latter element is present therefore, as is usually the case, it must be removed, or the indium extracted by a suitable procedure.

The composition of a typical zinc-base die-casting alloy, mazak alloy type A is given in Table I below:

TABLE I

Element	*Percentage content*
Aluminium	4.1
Magnesium	0.04
Iron	0.01
Copper	0.01
Lead	0.0028
Tin	0.001
Cadmium	0.0028
Zinc	Remainder

It was desired to determine indium in alloys of this type down to 0.0001% (1 p.p.m.) and it was therefore desirable to extract the indium from a large sample weight and to restrict the final volume to as small a value as possible. Alternatively the determination might be carried out directly upon a large sample weight dissolved in the smallest possible volume of solution.

The most recent study of the polarography of indium has been made by SCHUFLE, STUBBS AND WITMAN[2] who favour the mechanism:

$$\text{InCl}_4^- + 3e^- \rightarrow \text{In} + 4\,\text{Cl}^-$$

for trivalent indium in solutions of high chloride concentration. In 11.63N hydrochloric acid the half-wave potential is given as —0.772 V *versus* the saturated calomel electrode (S.C.E.). At lower chloride concentrations (less than 8M) the reduction becomes more irreversible. These authors were unable to confirm the value of —0.95 V *versus* S.C.E., given by LINGANE[3] for the reduction of indium perchlorate in perchloric acid, but they report a value of —0.573 V *versus* S.C.E. for 0.001N $\text{In(ClO}_4)_3$ in 0.1N perchloric acid. The standard electrode potential of In^{+3} is given by LATIMER[4] as —0.582 V *versus* S.C.E.

Other important methods for the determination of indium, such as that of MILNER[5], employ an extraction with 8-hydroxyquinoline into chloroform and subsequent polarography in a medium containing hydrochloric acid, sodium formate, hydrazine hydrochloride and starch. A half-wave potential of —0.6 V *versus* the mercury pool was reported. SINYAKOVA[6] measured the combined cadmium and indium step and then the cadmium step alone after precipitation of the indium with ammonium hydroxide. MAY AND HOFFMANN[7] extracted indium from a citrate–cyanide medium of pH about 8.5 by means of dithizone and cupferron. SAMERANO[8] has described a procedure in which a zinc solution containing traces of indium is shaken for half an hour with zinc oxide, when the indium is precipitated and may be removed by filtration.

The methods of SINYAKOVA and of MAY AND HOFFMANN appeared impracticable in view of the complexity of the alloys and no experimental work on them was therefore considered. A possible basis for a method was, however, provided by the fact that in an iodide base electrolyte cadmium is complexed but indium is unaffected. The cadmium step is therefore shifted to a point more negative than that of indium.

Before the applicability of the various methods, outlined above, was investigated, it was decided to study the possibility of a direct determination employing the derivative circuit of the linear-sweep cathode ray polarograph[9,10], since experiments had shown that this was capable of separating cadmium and indium waves provided there was no great disparity in their concentrations. This is described and discussed below.

EXPERIMENTAL

AnalaR zinc oxide was used as a source of zinc for these experiments and "specpure" indium oxide. In_2O_3 was used as the source of indium. A mazak alloy of approximately the composition given in Table I, above, was used for trials of the proposed methods.

All polarography was carried out at 25°C and *versus* the mercury pool anode. All potentials are quoted in the European sign convention. On this convention the saturated calomel electrode (S.C.E.) has been taken as +0.246 V *versus* the normal hydrogen electrode (N.H.E.).

A series of 20 ml solutions of zinc chloride was prepared, each containing 10 g zinc and various quantities of indium. These were polarographed using both the normal and derivative circuits of the cathode ray polarograph. The peak heights obtained were, in both cases, proportioned to the concentration of indium. The peak potential of the normal wave was —0.55 V *versus* the mercury pool and that of the derivate wave was —0.52 V.

It was found that on diluting the above solutions, the height of the peaks increased. Subsequent work was therefore carried out using diluted solutions containing 10 g zinc in 25 ml. In such solutions, doped with varying amounts of cadmium and indium, it was found that the indium wave was measurable on derivative working, provided that the cadmium : indium ratio was not greater than 10 : 1. The lowest concentration of indium that could be measured with the cathode ray polarograph set to maximum sensitivity corresponded to 1 p.p.m. of indium in the original sample. Normal and derivative polarograms of a typical indium-cadmium mixture are shown in Fig. 1, on which the method of peak height measurement on derivative working is shown.

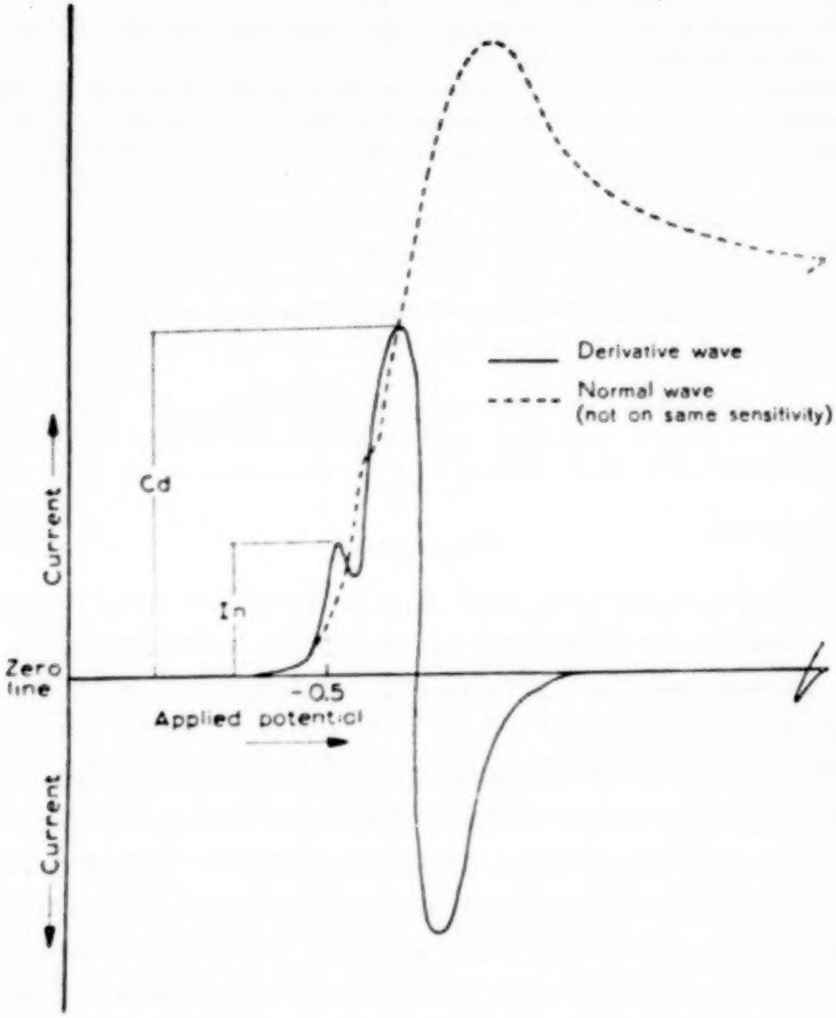

Fig. 1.

Calibrations carried out in the presence of 500 p.p.m. copper and 100 p.p.m. each of cadmium, tin and lead were satisfactorily linear and recoveries from solutions of mazak alloy, doped with indium were good. The method given below was therefore written. Typical recoveries are given in Table II below.

TABLE II

Sample details		*Cadmium (p.p.m.)**	*Indium (p.p.m.)**	
			added	*found*
Zinc oxide containing added cadmium and indium	1	100	12	10.9
	2	100	6	6.0
	3	100	3	—
	4	25	2.9	2.9
	5	10	1.0	0.8
Mazak alloy containing added indium	1	—	2.5	2.7
	2	—	4.0	3.7

* These quantities are calculated on the original sample weight

METHOD

Place 10.0 g of the alloy (as drillings or turnings) in a 400 ml beaker and add 45 ml 10*M* hydrochloric acid. When almost all the alloy has dissolved, heat to boiling and add 100 volume hydrogen peroxide until solution is complete. Evaporate to about 15 ml, transfer to a 25 ml calibrated flask and make up to volume with washings from the beaker.

Transfer a 3.0 ml aliquot of this solution to a polarographic cell and deoxygenate for 10 min by bubbling hydrogen or nitrogen through it.

Set the start potential control of the cathode ray polarograph to -0.30 V and, with the instrument set for derivative working and at an appropriate sensitivity setting, S_1, measure the height, h_1, of the indium peak which occurs at a potential of -0.56 V *versus* the mercury pool anode (see Fig. 1).

Add 0.10 ml of a standard indium solution* to the polarographic cell, stir for 30 sec** and measure the height, h_2, of the indium step under the conditions already described. Note the sensitivity setting, S_2, of the polarograph.

Calculate the indium content of the sample from the expression:

$$\text{p.p.m. indium} = \frac{10\ S_2h_1}{(3.1\ S_1h_2 - 3.0\ S_2h_1)}$$

DISCUSSION

The methods of SINYAKOVA[6] and MAY AND HOFFMANN[7] were discarded because, in the first case it requires the cadmium: indium ratio to be less than 5:1, which was unlikely. In the second case the extraction is rendered useless by the presence of aluminium and zinc in these alloys.

The increase in the heights of the polarographic peaks due to cadmium and indium on dilution of the solutions is considered to be due to a large decrease in the viscosity of the solution. This had been encountered elsewhere[11]. The precaution of working in slightly more dilute solution was sufficient to overcome the trouble.

The extent of the separation obtained with the derivative circuit was unexpected as previous experiments, carried out in 0.1*M* potassium chloride solution had indicated that the greatest cadmium : indium ratio that could be tolerated was 2:1 if merging of the derivative peaks was to be avoided. The improved resolution is attributed to the reversibility of the indium reduction in the high chloride concentration of the base electrolyte (about 6*M* zinc chloride).

The final method is applicable to most zinc alloys provided that the cadmium : indium ratio does not exceed 10:1. If this ratio is exceeded then the indium concentration may be reported as less than one tenth that of the determined cadmium content. It could be modified, without difficulty, to determine copper, lead and cadmium if this was desired.

In spite of the satisfactory nature of the method, special instrumentation, not yet generally available, is involved. It was therefore considered that other methods employing conventional polarography were also necessary and work to develop them was carried out. In the course of this work, which will be described in subsequent papers in this series, methods for the determination of indium in zinc and "aluminium-free" and "lead-free" zinc alloys, in addition to mazak, were developed.

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* The standard indium solution should be prepared as follows. Dissolve 0.0121 g pure indium oxide, or 0.010 g pure indium metal in 5 ml 10*M* hydrochloric acid. Transfer the solution to a 250 ml calibrated flask and make up to volume with water.

** Stirring is most conveniently carried out by passing a stream of bubbles of the gas used for deoxygenation.

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SUMMARY

The problems relating to the polarographic determination of trace amounts of indium in zinc and zinc-base alloys, especially mazak, are discussed and literature relating to the extraction and polarography of indium is briefly summarised. A method for the determination of indium using the linear-sweep cathode ray polarograph is presented and certain aspects are discussed.

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CURRENT INTEGRATION WITH PERMANENT MAGNET D.C. MOTORS IN CONTROLLED POTENTIAL COULOMETRIC ANALYSIS

by

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The rotational speed of a fixed field (permanent magnet) d.c. motor is, as a close approximation, linearly proportional to the energizing voltage over a wide range. Such a motor driving a revolution counter can be used to integrate voltage-time functions. Fig. 1 shows an excellent unit of this type manufactured by Electro Methods Ltd., Caxton Way, Stevenage, Herts, England, which is available with maximum input voltages of 1.5, 6, 12, or 24 V.

The capability of the Electro Methods integrator for integrating voltage-time functions has been discussed by WHEATLEY[1], who concluded that it functions accurately down to about 0.1 the nominal maximum voltage, *i.e.*, over a 10:1 range. With smaller input voltages the counting rate decays below the value corresponding to strict linearity with impressed voltage.

BETT, NOCK AND MORRIS[2] pointed out that the Electro Methods integrator can be used conveniently as a coulometer to integrate current in coulometric titrations. The current to be integrated as a function of time is passed through a precision resistor and the iR drop across this resistor actuates the integrator. Using a 1.5 V motor BETT *et al.* concluded that the accuracy of integration was ± 0.1% provided the input

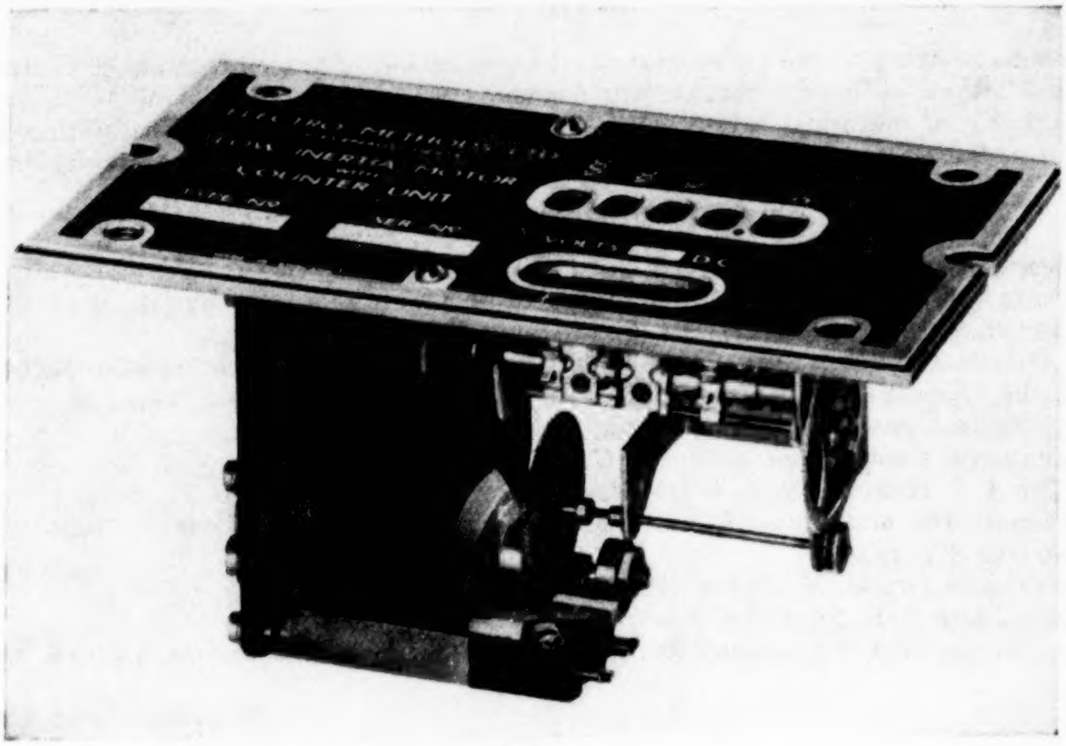

Fig. 1.

voltage *(iR)* was at least 0.25 V PARSONS, SEAMAN AND AMICK[3], who used a 24 V model of the Electro Methods integrator, also reported an accuracy of ± 0.1% when the voltage *(iR)* was at least 1/5 the maximum input voltage. These studies convincingly demonstrated the convenience and high accuracy of this integrator in coulometric titrations in which the current varies only slightly, but they also suggest that significant negative errors will result if the current (input voltage) varies over more than a 5:1 range.

In the present study it was found that correction for the decay of the counting rate of the Electro Methods integrator at relatively small input voltages can easily be made, and consequently the useful range of the instrument (± 0.3% error) can be extended to 100:1. This permits the use of the instrument as an exceedingly simple and accurate coulometer in coulometric analyses at controlled potential[4] in which the current may decay over a 100:1 or larger range. The coulomb capacity of the instrument can be varied widely simply by appropriate choice of the resistor in which the iR drop which energizes the integrator is generated.

Table I shows typical data that were obtained in testing the performance of the 24 V model (Type 913) Electro Methods integrator as a coulometer over a 200:1 range of current. All the data were obtained with a constant shunt resistance R of 90 ohms (± 0.1%). The current i was held constant at each value to ± 0.02% by the regulator previously described[5]. Time was measured with a Standard Electric Time Co. Model S-10 electric stopclock (precise to ± 0.01 sec) driven by the local commercial 110 V, 60 cycle supply whose frequency variation was known to be smaller than ± 0.1%. The time of each trial was selected to provide a large enough accumulated reading of the counter, N, for accurate measurement. The data were accumulated randomly on different days.

If the counting rate N/t were strictly proportional to input voltage (iR) then

$$N = k'\, iRt \qquad (1)$$

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TABLE I

CALIBRATION DATA FOR ELECTRO METHODS LTD.
INTEGRATOR TYPE 913 (24 V)

Shunt resistance = 90 ohms

i amp	iR volts	N counts	Time sec	$\frac{N}{iRt}$ counts/sec/V	$\left(\frac{N}{iRt} + \frac{0.0032}{iR}\right)$ counts/sec/V
0.27180	24.462	940.5	500.1	0.07690	0.07703
.22290	20.061	308.9	200.0	.07699	.07715
.18294	16.465	316.7	250.0	.07694	.07713
.11050	9.945	321.5	420.0	.07697	.07729
.06786	6.107	235.1	500.0	.07699	.07751
.027118	2.440	371.6	2000.0	.07613	.07744
.013586	1.223	156.0	1700.0	.07507	.07768
.006789	0.611	91.0	2060.0	.07230	.07753
.004528	0.408	181.0	6420.0	.06918	.07703
.002719	0.245	47.2	3010.0	.0641	.0772
.001359	0.122	20.1	3280.0	.0501	.0763
				Av. (except last)	0.0773 ± 2

or the quantity N/iRt, equal to k', should be constant over the entire range of current. From Table I it is seen that this quantity is constant to about ± 0.1% only over the 4:1 range from $i = 0.27$ to $i = 0.068$ amp. With smaller values of i (or iR) this pseudo constant decreases more and more rapidly, until with the smallest usable input voltage corresponding to $i = 0.001$ amp it has become 35% smaller than the value at the maximum input voltage.

Examination of these data revealed that the decay of k' with decreasing input voltage is, as a very close approximation, inversely proportional to the input voltage iR, according to the relation

$$k' = k - \frac{\beta}{iR} \qquad (2)$$

The constant β was evaluated empirically, and for this particular unit was found to be 0.0032 counts/sec with a shunt resistance of 90 ohms.

The correctness of eqn. (2) is demonstrated by the constancy over the entire usable range of input voltage of the values of $k' + (0.0032/iR)$ in the last column of Table I. Consequently in place of eqn. (1) we have

$$N = \left(0.0773 - \frac{0.0032}{iR}\right) iRt \qquad (3)$$

This relation is correct to ± 0.3% over a 100:1 range of input voltage, and even with an input voltage as small as 1/200 of the maximal value it is in error by only —1.3%.

Measurements were also made with a 10 ohm and with a 1000 ohm shunt resistance, using appropriate current ranges so that the maximum value of iR was 24 V. In both cases an equation of the same form as eqn. (2) was obtained, and the counting rate at the maximal value of iR was very nearly the same as with the 90 ohm resistance. With the 10 ohm resistance the constant β in eqn. (2) was close to the value observed with the 90 ohm resistance, but with the 1000 ohm resistance it was approximately twice as great. With this particular model of the integrator the optimum range of shunt resistance appears to be from about 10 to 200 ohms, corresponding to maximum currents from about 2.4 to 0.12 amp.

From eqn. (3), the relation between the quantity of electricity in coulombs, Q, and the counter reading N, for this particular instrument with a 90 ohm shunt resistance, becomes

$$Q = \int_0^t i dt = \frac{N + 0.0032\ t}{0.0773\ R} \quad \ldots\ldots\ldots\ldots\ldots \quad (4)$$

The use of this relation requires that the time of an experiment be noted in order to apply the correction 0.0032 t, but this is so simply done that eqn. (3) is very nearly as convenient as the much more restricted and far less accurate relation $Q = N/k'R$ usually assumed. Presumably, the other models of the Electro Methods integrator with smaller input voltage will obey an equation of the same form as eqn. (4).

The characteristic constants k and β for each integrator must, of course, be evaluated by obtaining calibration data like those in Table I. However the counting rate for all instruments of this type presumably will obey a relation of the form of eqn. (2) so that calibration with only two or three widely different currents should suffice at each value of the shunt resistance. Some progressive change in the characteristic constants with time of use is to be expected, and periodic recalibration is advisable.

The temperature coefficient of k' is about 0.035%/deg. The integrator should not be mounted near iron or other magnetic material because this can produce a significant change in the calibration factor.

In employing these integrators as coulometers in controlled potential coulometric analysis, the resistance R should be selected so that the input voltage iR will be nearly the maximal permissible value at the start of the electrolysis. In most cases the current does not decay completely to zero but rather to a small background current[4]. The range of current decay ordinarily is between about 100:1 and 500:1. Under these usual conditions the Electro Methods integrator can evaluate Q via eqn. (4) with an error not greater than about —0.3%.

SUMMARY

The negative deviation from linearity of the applied voltage-counting rate curve of a permanent magnet d.c. motor integrator (Electro Methods integrator) at small input voltages is inversely proportional to the applied voltage. Correction for this can easily be made, and when this is done such an integrator is capable of an accuracy of the order of ± 0.3% over a 100:1 range of input voltage. The Electro Methods integrator is ideally suited as a coulometer in controlled potential coulometric analysis.

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4-AMINO-4′-CHLORODIPHENYL AS ANALYTICAL REAGENT FOR SULPHATE

by

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In the ultimate micro-analysis of organic compounds there is a great need for a reliable and convenient method for the determination of sulphate in amounts of a few mg. While searching for such a method we have tried out various reagents, amongst which was the new reagent, 4-amino-4′-chlorodiphenyl, proposed by BELCHER, NUTTEN AND STEPHEN[1]. Although strictly adhering to the recommended procedure we obtained inconsistent and low results. Similar experiences have been reported by BAUMINGER[2], and in a short communication GEILMANN AND GEBAUHR[3] state that the excellent results[1] obtained with the reagent are due to a compensation of errors, the losses resulting from incomplete precipitation and washing the precipitate being balanced by adsorption of the reagent by the precipitate. Recently, BELCHER and co-workers[4] have reported that the solubility of the freshly precipitated amine sulphate appears to be higher than was first estimated for the dried material[5].

On reviewing the papers on the method[1-7], little useful information could be gained for estimating whether this reagent is theoretically suitable for the above-mentioned determination. The only two papers containing the appropriate data are those published by BELCHER and co-workers[4,5], who determined the solubility of the amine sulphate in water and the sensitivity of the reagent towards sulphate. From the solubility data given in the first paper[5], the solubility product is less than 10^{-13} if the pH of the saturated solution is high enough to justify the approximation that all the sulphate present occurs as divalent sulphate ions, and if solution proceeds normally. From the diagram given in the second paper[4] and assuming the ionisation constant of HSO_4^- to be $1.2 \cdot 10^{-2}$ and using the Debye-Hückel formula[8] for estimating the mean activity coefficients, the solubility product is calculated to be between $1.3 \cdot 10^{-11}$ and $2.3 \cdot 10^{-11}$. The figures for the estimated solubility product of 4-amino-4′-chlorodiphenyl sulphate are found to differ by a factor of 10^2. The uncertainty in the estimation of the activity coefficients could not account for this large discrepancy, and, according to our observations, the crystals are of the soft type; practically no supersaturation is to be expected nor has any been observed.

In view of the foregoing it was decided to make an experimental determination of the quantities governing the equilibrium of the system 4-amino-4′-chlorodiphenyl sulphate–water. The ionisation constant and the solubility of the amine were determined, and the solubility of the amine sulphate was redetermined. It was found that the reported figure for the solubility of the amine sulphate is about ten times too low, thus explaining the discrepancy mentioned. As will be shown later, the technique used by BELCHER and co-workers[5,6] in the determination of the solubility gave erroneous results due to the fact that the amine itself has a very low solubility in water. The solubility data now reported are in reasonable agreement with the data from the experiments in the second paper[4] by the authors cited.

EQUILIBRIUM CONDITIONS FOR THE SYSTEM AMINE SULPHATE–WATER

If B stands for the amine, the following reactions will take place when the corresponding sulphate $B_2H_2SO_4$ dissolves in water:

$$B_2H_2SO_4 = 2\,BH^+ + SO_4^{-2} \quad \text{(1)}$$

$$BH^+ + H_2O \rightleftarrows B + H_3O^+ \quad \text{(2)}$$

$$HSO_4^- + H_2O \rightleftarrows SO_4^{-2} + H_3O^+ \quad \text{(3)}$$

We shall assume that the pH of the saturated solution is high enough for the equilibrium (3) to be completely displaced to the right. For 4-amino-4′-chlorodiphenyl sulphate an estimate of the pH from the value for the solubility[5], if correct within a factor of ten, shows that this assumption is approximately valid. The following relations then hold:

$$\frac{[H^+]\cdot[B]}{[BH^+]} = k_a = K_a \cdot f_{BH^+} \cdot (f_{H^+})^{-1} \quad \text{(4)}$$

$$[BH^+] + [H^+] = 2\,[SO_4^{-2}] \quad \text{(5)}$$

$$[BH^+]^2 \cdot [SO_4^{-2}] = k_s = K_s \cdot (f_\pm)^{-3} \quad \text{(6)}$$

where K_a is the acidic dissociation constant of the cationic acid BH^+, f the activity coefficient, and K_s the thermodynamic solubility product of the amine sulphate. Equation (5) is obtained from the condition of electroneutrality. From equations (4) to (6) one finds

$$[SO_4^{-2}] = \left\{1/4\,k_s\,(1 + k_a/[B])^2\right\}^{1/3} \quad \text{(7)}$$

On shaking the amine sulphate with water it will dissolve, and the pH will decrease until sufficient BH^+ and SO_4^{-2} ions have been generated for equation (6) to be fulfilled. However, if the amine happens to be only sparingly soluble, so that its solubility is exceeded before the final equilibrium is attained, the amine starts to precipitate and [B] assumes a constant value in the solution. At equilibrium the concentration of sulphate ions is then given by equation (7). The same state of equilibrium will obviously be reached if sulphuric acid of greater concentration than that given for sulphate in equation (7) is treated with an excess of the amine. This behaviour of an amine salt is well known in the case of diphenylamine picrate[9], but it has not been appreciated that it gives rise to certain problems in the determination of the solubility of amine salts. The technique used by BELCHER *et al.*[6] for the determination of the solubility of amine sulphates, *i.e.* taking a fixed volume of the saturated solution to dryness and weighing, may in certain cases lead to erroneous results. When this fact is realised, adequate precautions can be taken to avoid the risk of this source of error.

The improved technique for the determination of the solubility of 4-amino-4′-chlorodiphenyl sulphate is described in detail in the experimental part. The new value for the solubility, 164 mg per litre, is completely at variance with the value previously reported[5]. It was found that one litre of the saturated solution of the amine sulphate contains 325 μmoles of SO_4 and 200 μmoles of the amine, *i.e.* a deficit of 450 μmoles of the amine, which has precipitated during the process of the dissolution. That the error in the first estimation is due to the factors discussed and not to some other factor, such as the age or the condition of the precipitate[4], can furthermore be shown by comparison with the solubility of 4-aminodiphenyl sulphate. A redetermination using the modified technique gave results (120 mg/l at 20°C) in complete agreement with the determination by BELCHER *et al.*[6] (130 mg/l at 25°C). From the estimated solubility of the amine ($7 \cdot 10^{-4}$ moles/l) and the pK^a (4.33) it can be shown that in this case no objections can be raised against the technique used by BELCHER *et al.*

EXPERIMENTAL

Preparation of 4-amino-4'-chlorodiphenyl

The amine was prepared at the Department of Organic Chemistry at the University of Uppsala by the courtesy of Prof. ARNE FREDGA and in the same manner as described by BELCHER and co-workers[5]. It was further purified three times by precipitation with sodium hydroxide from the filtered solution in $0.05 M$ hydrochloric acid. It was finally recrystallised from light petroleum, boiling range 60 to 80°, and dried *in vacuo*. M. p. 131°. Ultimate analysis:
N (6.88%): 6.86 ± 0.02%; Cl (17.41%): 17.33 ± 0.06%.

Ionisation constant of 4-amino-4'-chlorodiphenyl

The solubility of the amine was found to be too low to permit a direct determination of the ionisation constant in any of the usual ways. Instead, the acidic dissociation constant K_a of the corresponding cationic acid, BH^+, was determined by a spectrophotometric method[10], based upon the fact that the absorption band of the amine at 279 mμ is shifted towards a shorter wavelength, 254 mμ, as the amine is ionised. In Fig. 1 an example of such a determination is shown. The three curves represent the absorption of the completely ionised amine (curve *a*; pH = 1.3), the un-ionised amine (curve *b*; pH = 10), and the partly ionised amine at an intermediate pH (curve *c*; pH = 4.17); the total concentration of amine was in all three cases the same, *viz.* 19.0 μmoles/l. It can easily be shown that for a solution corresponding to curve *c*, the following relation holds:

$$\frac{[BH^+]}{[B]} = \frac{A_b - A_c}{A_c - A_a} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

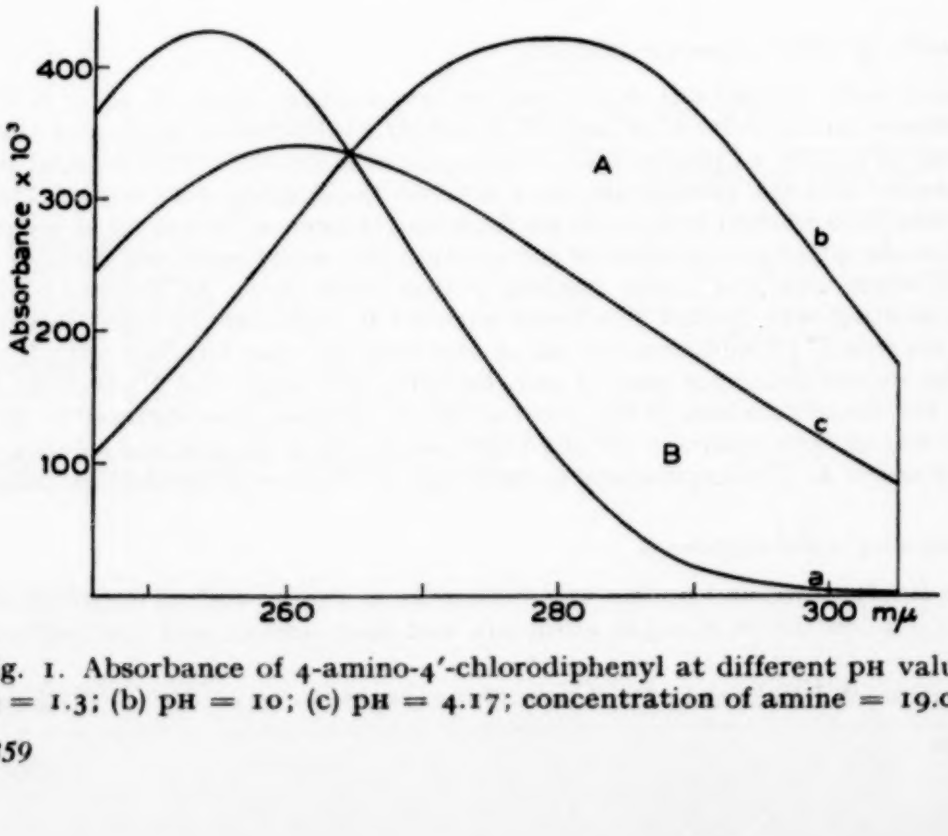

Fig. 1. Absorbance of 4-amino-4'-chlorodiphenyl at different pH values.
(a) pH = 1.3; (b) pH = 10; (c) pH = 4.17; concentration of amine = 19.0 μmoles/l.

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where A_a, A_b, and A_c are the absorbances of the solutions corresponding to curves *a*, *b*, and *c*, respectively, as measured at a specified wavelength. The ratio $[BH^+]:[B]$ was thus found simply by drawing the three curves on graph paper, cutting out and weighing the areas designated A and B in Fig. 1. Then from equation (4)

$$pK_a = (\text{pH})_c + \log A/B + \log f_{BH^+} \quad \ldots\ldots\ldots\ldots\ldots \quad (9)$$

The activity coefficient f_{BH^+} was calculated according to the Debye-Hückel formula in the approximate form given by GUGGENHEIM AND SCHINDLER[8].

The determination was actually carried out in the following way. 45 to 50 mg of the amine was accurately weighed into a 250 ml volumetric flask and dissolved by heating in 10.00 ml of $0.1000M$ hydrochloric acid. The hot solution was diluted to about 200 ml and after cooling made up to volume. The absorbances of the following solutions were then recorded, all the solutions being made up to 100 ml before the measurement. (a) 4 ml of the test solution + 5 ml of $1.00M$ hydrochloric acid; (b) 4 ml of the test solution + 4 ml of $0.50M$ ammonia; (c) 4 ml of the test solution + 10 ml of acetate–acetic acid buffer solution, pH = 4.17, and ionic strength, $\mu = 2 \cdot 10^{-3}$, at tenfold dilution. In the first tentative experiment no buffer solution was used. The pH of solution c could then be estimated from the amount of hydrochloric acid added to the original test solution, and an approximate value for pK_a could be found. The pH was then recalculated and found to be 4.15. The buffer solution was then prepared as stated to give maximum buffer capacity. Another buffer solution, pH = 4.65 and $\mu = 5 \cdot 10^{-3}$ at tenfold dilution, was used in one single experiment. The calculated and measured pH values of the buffer solutions agreed within ± 0.02 pH units when checked against N.B.S. pH standard $0.05M$ potassium hydrogen phthalate. All experiments were carried out in a constant-temperature room at 20 ± 0.2°. The essential data and results of the experiments are collected in Table I.

TABLE I

pK_a OF 4-AMINO-4′-CHLORODIPHENYL AT 20°

Expt. No.	*Concentration of amine µmoles/l*	*(pH)c*	*log A/B*	*pka*	*pKa*
8	20.64	4.17	0.07	4.24	4.22
9	18.09	4.17	0.07	4.24	4.22
9b	18.09	4.65	—0.41	4.24	4.21
10	19.44	4.17	0.06	4.23	4.21
11	19.02	4.17	0.06	4.23	4.21
Mean	—	—	—	—	4.21

Solubility of 4-amino-4′-chlorodiphenyl sulphate

The experiments were carried out in a constant-temperature room at 20 ± 0.2°. In series A, 300 mg of the amine was dissolved in 100 ml of $0.05M$ hydrochloric acid, and the solution was poured into 10 ml of $0.05M$ sulphuric acid. The liquid was drawn off by a small porcelain filter stick, and the beaker and the precipitate were washed thoroughly with water. The precipitated amine sulphate was then washed into a 250 ml flask and shaken with 250 ml of water in a Wagner shaking apparatus. At intervals a portion of the solution was withdrawn and titrated with standard alkali. The equilibrium was practically reached within three days. At the end of the experiment a portion of the solution was diluted five times with $0.1M$ hydrochloric acid, and the absorbance at 254 mµ was recorded. In addition, 50 ml of the solution was titrated with $0.01M$ standard alkali against the mixed indicator phenol red–bromthymol blue; the titrimetric determination was checked by the determination of sulphur by the methylene blue method*[11]. In series B, 200 mg of the amine was shaken with 250 ml of $10^{-3}M$ sulphuric acid, and the solution was analysed at intervals as in series A. The experimental data and results are presented in Table II.

Solubility of 4-amino-4′-chlorodiphenyl

100 mg of the finely powdered amine was shaken as in the preceding experiment with 100 ml of water, to which a few drops of $0.5M$ ammonia had been added, and the concentration of the

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* The author is much indebted to Dr. LILLY GUSTAFSSON for carrying out these determinations.

TABLE II

SOLUBILITY OF 4-AMINO-4′-CHLORODIPHENYL SULPHATE IN WATER AT 20°

Expt. series	*pH*	$[SO_4^{-2}]$ *μmoles/l*		$[BH^+] + [B]$ *μmoles/l*	$[BH^+]$ *μmoles/l*	*Solubility product* K_s
		a	*b*			
A	3.4	319	319	202	179	—
	3.4	318	—	203	180	—
B	3.4	330	329	198	175	—
	3.4	333	—	199	176	—
Mean	3.4	325	324	200	177	$0.82 \cdot 10^{-11}$

a By titration.
b By methylene blue method.

amine in the solution was determined spectrophotometrically at intervals. The equilibrium was practically reached within 3 days. The molar solubility of the amine at 20° was found to be $2.28 \cdot 10^{-5}$. It can also be calculated from the data obtained in the previous experiment (Table II); one then finds the value $2.31 \cdot 10^{-5}$.

Solubility of benzidine sulphate

As no data on the solubility of benzidine sulphate at 20° seem to be available, it may be of interest to report this determination also. The same technique was used as for 4-amino-4′-chlorodiphenyl sulphate (series A). The spectrophotometric (247 mμ) and titrimetric determinations agreed within ± 1%, as could be expected from the fairly good solubility of benzidine in water. For the molar solubility at 20°, the value found was $2.84 \cdot 10^{-4}$. From the reported pK_b values of benzidine, 9.03 and 10.25, respectively[12], the solubility product K_s of benzidine sulphate at 20° is calculated to be $2.8 \cdot 10^{-8}$.

DISCUSSION

The results of the experimental work are collected in Table III. The discussion will be confined to the use of 4-amino-4′-chlorodiphenyl as a reagent in the determination of sulphur by ultimate organic micro-analysis. With regard to the accuracy attainable in the various steps of the micro-analytical procedure, it seems reasonable to state

TABLE III

SUMMARY OF EXPERIMENTAL RESULTS

	4-amino-4′-chlorodiphenyl	*Benzidine*
Solubility in water at 20°:		
Solubility of amine, molar	$23 \cdot 10^{-6}$	—
Solubility of amine sulphate:		
as amine sulphate, molar	$325 \cdot 10^{-6}$	$284 \cdot 10^{-6}$
as amine sulphate, mg/l	164	80
as SO_4 , mg/l	31	27
Solubility product K_s of amine sulphate at 20°	$0.82 \cdot 10^{-11}$	$2.8 \cdot 10^{-8}$
pK_a at 20°	4.21	—
Absorptivity, molar:		
at 254 mμ; pH $\leqslant 1.3$	$2.23 \cdot 10^4$	—
at 279 mμ; pH $\geqslant 10$	$2.21 \cdot 10^4$	—
at 265 mμ; isobestic point	$1.75 \cdot 10^4$	—

that the error introduced in the final isolation and determination of 2.5 to 5 mg sulphate from an initial volume not exceeding 50 ml, should be less than 1%.

BELCHER and co-workers[4] recommend a final concentration of the reagent of 0.12% or greater when determining 2.5 to 20 mg of sulphate in a final volume of 100 ml, and state that under these conditions "the amount of sulphate left in solution is insignificant". From their data it is seen that the losses may amount to 50 µg sulphate. From the solubility product of the amine sulphate, $0.8 \cdot 10^{-11}$, the corresponding figure is calculated to be 30 µg. In the range here discussed the losses due to incomplete precipitation cannot merely be neglected. For a more precise estimate of these losses and their adverse effect upon the accuracy of an actual analysis, additional experiments are necessary. It should, however, be emphasised that the error introduced may be considerably reduced under certain conditions (see below).

The solubility of 4-amino-4'-chlorodiphenyl sulphate was found to correspond to 31 µg SO_4/ml. It is thus even larger than that of benzidine sulphate, the corresponding value being 27 µg SO_4/ml. In washing the precipitate it should be borne in mind that the reagent is adsorbed by the precipitate to a certain degree[3] and that the pad of pulp used in the filtration is apt to increase the difficulties due to adsorption phenomena[2]. Even though the difficulties due to the filter pulp may be partly avoided[2], the washing procedure seems to be very critical. This point of view is in full accord with the statement of GEILMANN AND GEBAUHR[3], quoted in the introduction. To cope with the difficulties actually encountered, BAUMINGER[2] has suggested that a saturated solution of the amine sulphate should be used in washing the precipitate. Accordingly, in a series of recovery tests BAUMINGER has obtained an accuracy of about ±3 µg sulphate in six determinations of 1.5 mg sulphate. It is known that the method of washing with a saturated solution of the precipitate at best leads to a compensation of errors when adhering to a carefully worked out scheme. The very excellent results obtained by BAUMINGER should be regarded in the light of this fact. The demand on the skill of the analyst in such a procedure can be judged only from an estimate of the relative magnitude of the accuracy aimed at and the errors involved in the compensation process. Summing up, it seems necessary to gather more experimental experience, especially as to the magnitude of the errors introduced in the various steps of the procedure, before deciding upon the general suitability of the reagent for the isolation of sulphate in amounts occurring in organic micro-analysis.

Regarding the general use of the reagent the following may be observed. It is prescribed[4] that the $0.01M$ reagent solution and the test solution should both be $0.05M$ with respect to hydrochloric acid. From a consideration of the pK_a and the solubility of the amine, it should be possible to reduce the excess of the hydrochloric acid in the reagent solution to a half, the concentration of BH^+-ions being practically unaffected. Using this reagent solution, and where possible neutralizing the test solution beforehand, would favour the completeness of precipitation by a factor of two or three owing to the increased pH and lower ionic strength of the solution. The pH of the final solution should not be increased further or the amine will precipitate.

SUMMARY

The acidic dissociation constant and the solubility of 4-amino-4'-chlorodiphenyl have been determined. The solubility of the amine sulphate has been redetermined and found to be ten times greater than reported earlier. The reason for the discrepancy is revealed, and the use of the amine as a

reagent in the micro-analytical determination of sulphate is discussed in the light of the experimental results.

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COMPLEXES OF GOLD(III) AND TITANIUM(III) WITH 8-HYDROXYQUINOLINE

by

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INTRODUCTION

During the past few years biochemical experiments in these laboratories made necessary the separation of the valency states of a number of cations by paper chromatography[1,2]. This led to the preparation of 8-hydroxyquinoline (oxine) complexes of metals in lower valency states[2]. In view of the interesting natures of the cuprous and argentous complexes, it was decided to investigate the existence of 8-hydroxyquinoline compounds with Au. The only oxine derivative of gold which, to the author's knowledge, has been reported is a complex of oxine-2-carboxylic acid which was described as purple in colour[3], but was not apparently further studied.

The chromatography of the valency states of Ti for biochemical purposes furnished evidence for the existence of an unstable Ti(III) - oxine complex.

EXPERIMENTAL

Gold(III)

From gold chloride and oxine, under certain conditions, an apple-green complex was prepared. The gold chloride was obtained by dissolving metallic gold in "aqua regia" and evaporating the solution gently to dryness. Chloroauric acid as supplied by British Drug Houses Ltd. was also found to be satisfactory starting material. The complex was produced (1) by dissolving gold chloride in a minimum quantity of warm pyridine and precipitating pyridine-gold chloride compounds from the solution by the addition of excess ether. The precipitate was washed with ether twice by decantation and allowed to stand in contact with either a saturated ethereal solution of oxine for 24 h or a saturated acetone solution of oxine for 5 h. (2) by adding solid oxine to a solution of gold chloride in ethanol, cooled to 0°C, and allowing the mixture to stand for several hours. The reaction was greatly accelerated by adding approximately ¼ of the volume of pyridine to the mixture (NH_3 gas did not yield the same result). A similar effect occurred with a mixture in acetone medium, in which there appeared to be little or no reaction prior to the addition of pyridine. A solution of gold chloride in ethanol which had been kept for several days was sometimes observed to give a better product than a solution that had been freshly prepared. (3) by adding an excess of an ethereal solution of oxine to a solution of gold chloride in ether and allowing the precipitate (which was sometimes dark brown initially) to stand in contact with the mixture for 24 hours.

The green precipitates obtained by the above methods were filtered (Büchner funnel, Whatman No. 541 filter-paper) and washed with ether, water, ethanol and ether. If the solid had a yellowish tinge at this stage it was shaken with cold ethanol and filtered and washed again, and finally dried *in vacuo* over P_2O_5 in a desiccator. The complex was a dark green powder which melted with decomposition at 155° and dissolved to a limited extent in acetone and chloroform but was insolube in ether and water. Saturated chloroform solutions of the samples prepared by the methods described were examined spectrophotometrically over the range 300-700 mμ. All showed identical absorption graphs, namely, an intense peak at 400 mμ with a much shallower peak at 580 mμ, and troughs at 340 mμ and 480 mμ (see Fig. 1).

The compound did not fluoresce in U.V. light.

The gold content was determined by dissolving a known weight of the complex in hydrochloric acid, precipitating the metal with hydroquinone and filtering and ashing the precipitate, and also by the direct ashing of a sample of the complex. The mean value (% Au) of 4 determinations was 46.5 ± 0.3. Small variations were found in the non-metallic contents of the complex, depending upon the method of preparation. A sample prepared from gold chloride and oxine in ethanolic medium gave C, 27.5; H, 1.5; N, 3.6; Cl, 17.3, while a specimen obtained via pyridine-gold chloride gave C, 27.2; H, 1.7; N, 3.5; Cl, 18.4 (possibly some "undisplaced" Cl, see below). These results, which were reproducible, approach the values required for the formula $AuCl_2 \cdot C_9H_6ON$ namely: Au 47.8; C, 26.2; H, 1.5; N, 3.4; Cl, 17.2.

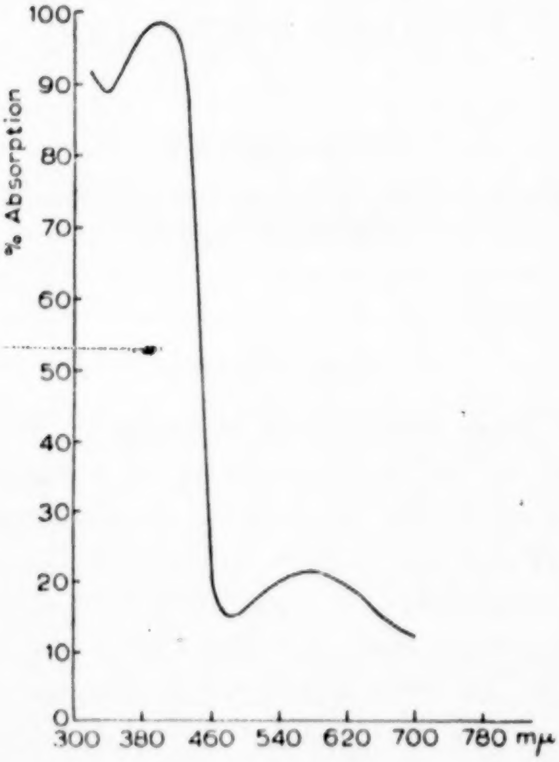

Fig. 1. Absorption spectrum of Au-8-hydroxyquinoline complex.

Analogous experiments, conducted in an atmosphere of CO_2, with aurous chloride (prepared by heating $HAuCl_4$ to 196°-198° in a stream of dry CO_2) and oxine yielded no evidence for the existence of an aurous-oxine complex.

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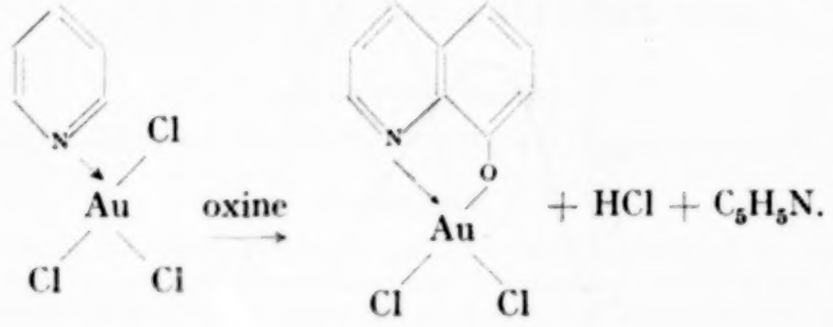
The facilitation of the reaction between gold chloride and oxine by pyridine prompted an investigation into the action of oxine upon the compounds $AuCl_3{\cdot}C_5H_5N$ and $AuCl_3{\cdot}2C_5H_5N$ which were first described by Francois[4]. The pale yellow monopyridine complex was prepared by treating the precipitate obtained by the addition of ether to a solution of $HAuCl_4$ in pyridine with warm water. After filtering off, the product was recrystallised from water and dried in vacuo over P_2O_5. Found: Au 51.4, N 3.5. Calc. for $AuCl_3{\cdot}C_5H_5N$ Au 51.4, N 3.66. The orange dipyridine compound was obtained by the method of Francois[4] by allowing a concentrated solution of $HAuCl_4$ in warm dry pyridine to crystallise, and filtering off and drying the crystals. Each of the compounds was allowed to stand in contact with saturated solutions of oxine in acetone and in ether. With an acetone solution the monopyridine complex (which dissolves easily in acetone) was rapidly converted to a good sample of the green oxinate, but the action upon the dipyridine compound was very slow. A similar effect was noted using an ethereal solution of oxine, but the reaction was much slower than with an acetone solution, possibly because of the smaller solubility of the monopyridine complex in ether.

It has been stated[5] that the monopyridine compound is the non-ionized complex $(AuCl_3{\cdot}C_5H_5N)^{\circ}$, while the dipyridine complex contains a monovalent cation thus: $[AuCl_2{\cdot}(C_5H_5N)_2]^+\ Cl^-$. Oxine possibly reacts with the monopyridine complex displacing pyridine and one Cl atom according to the suggested scheme:



but the dipyridine entity appears to be much more resistant to the action of oxine.

Titanium(III)

Attempts to separate Ti(IV) and Ti(III) upon paper strips by downward chromatography resulted in only a partial resolution although 136 different solvent mixtures were examined as eluants. As is well known, the Ti^{+3} ion is reasonably stable, but in covalent combination trivalent Ti is readily oxidised to the tetravalent state. Limitations were therefore imposed upon the eluant employed for the separation, as a high water content and the presence of a strong mineral acid was necessary to prevent the oxidation of Ti(III) on the strip. This meant that the use of "buffers", weak acids, and/or organic chelating agents was precluded.

The most satisfactory eluant consisted of acetone, water and sulphuric acid (95 : 20 : 2.5 by volume) and for a 10 cm run the R_F values (centre of zones) were approximately Ti(III) 0.6, and Ti(IV) 0.4. The chromatograms were developed by spraying them with a slightly acid solution of Na_2MoO_4 which revealed Ti(III) as a blue zone ("Mo blue"). A fresh chromatogram was then dipped into a solution of oxine in ether and after drying it the strip was exposed to NH_3 gas. Ti(III) showed as a green zone, gradually turning orange and Ti(IV) appeared as an orange zone. By marking the zones shown up by these tests and superimposing the strips upon one another, it was possible to determine the presence or absence of Ti(III) or Ti(IV).

The appearance of a transient green colour when a Ti(III) spot was treated with oxine suggested the formation of an unstable 8-hydroxyquinoline complex of trivalent Ti. When a solution of $TiCl_3$ was treated with ethanolic oxine in an atmosphere of CO_2 according to the following method, a bright green solid was precipitated:

A solution of Fe-free titanous chloride* containing about 12.5% w/v $TiCl_3$ was treated with a little sodium amalgam and filtered (Whatman No. 42 paper). 2 ml of the filtered solution was added to 100 ml of water in a wide mouth bottle from which air had been displaced by CO_2. A swift flow of CO_2 was maintained and 25 ml of a cold saturated solution of oxine in ethanol was added to the contents of the bottle. The vessel was allowed to stand in water at 50° (CO_2 flow maintained) until the green solid had flocculated (5 min). The delivery tubes were then withdrawn and the bottle closed by a tightly fitting rubber bung. The precipitate was centrifuged (2500 r.p.m. for 10 min) and the supernatant liquid removed by replacing the delivery tubes and blowing the liquid out of the bottle by reversing the flow of CO_2. The supernatant liquid was shown to be free of Ti (acidification with HCl and addition of H_2O_2) and the solid, when dissolved in 5*N* HCl in the bottle (CO_2 atmosphere) formed a strongly-reducing solution (liberation of Ti^{+3} ions) which reduced Na_2MoO_4 to "Mo-blue". The green solid was not obtained in the dry state as it appeared to be decomposed by

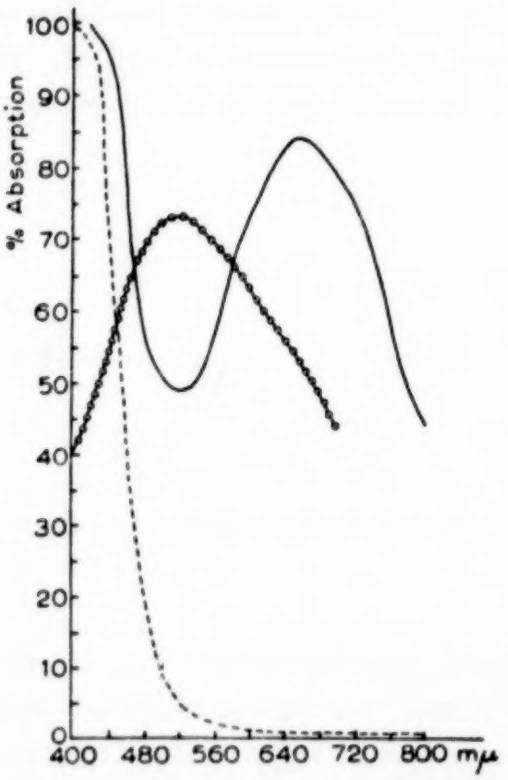


Fig. 2. Visible spectra of Ti-8-hydroxyquinoline complexes.
—— Ti(III) complex ---- Ti(IV) complex -o-o-o-o- $TiCl_3$ in ethanol.

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* Ti solutions were freed from Fe by oxidising them to the tetravalent state with H_2O_2 and then separating Ti(IV) and Fe(III) by standard cellulose column technique using a mixture of acetone, ethanol, HCl and water (75:20:5:5 by volume) as the eluant. After the expulsion of the Fe band, elution of Ti(IV) was continued with 2*N* HCl. The Ti fraction was concentrated by distillation under reduced pressure, and was reduced to the trivalent state by treatment with sodium amalgam in an atmosphere of CO_2.

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washing with dehydrating solvents (*e.g.* acetone) and was extremely sensitive to oxidation being converted to the orange Ti(IV) complex within a period of 15-30 seconds. Because of these properties, a reliable analysis of the compound could not be obtained.

The spectrophotometry of the green complex, which did not appear to fluoresce in U.V. light, was successfully studied in an atmosphere of CO_2 in a modified Thunberg tube which was fused to a 1 cm silica spectrophotometric cell[6].

5 ml of a 1% w/v solution of oxine in ethanol was placed in the cell, and 0.1 ml of a 1% w/v solution of $TiCl_3$ (prepared by reducing a solution of $TiCl_4$ in 5*N* HCl with Na amalgam in an atmosphere of CO_2, filtering and diluting the solution with water) pipetted into the side arm of the tube. The air in the vessel was displaced by CO_2 delivered through a capillary tube which passed under the surface of the oxine solution in the cell. The capillary tube was then withdrawn, the vessel stoppered securely and the two solutions mixed by inverting the Thunberg tube several times. An absorption graph for the Ti(III) complex was plotted over the range 400-800 mμ (Fig. 2). Air was then allowed access to the mixture by removing the stopper, and when the solution had changed in colour from green to yellow, a graph was plotted for the Ti(IV) complex. A curve was also constructed for a solution of $TiCl_3$ in ethanol. The Ti(III) complex showed an absorption maximum at 660 mμ and a minimum at 520 mμ while a maximum at 520 mμ was observed for $TiCl_3$. The spectrum of the Ti(IV) complex showed no peak in the visible range.

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SUMMARY

The preparation of an 8-hydroxyquinoline complex of trivalent gold by the action of oxine upon gold chloride and "monopyridine gold chloride" is described. The absorption spectrum of the complex, which approximated to the composition $AuCl_2 \cdot C_9H_6ON$ was plotted in the U.V. and visible regions of the spectrum.

A partial separation between tri- and tetravalent titanium was obtained using paper chromatography. Absorption curves were obtained for oxine complexes of Ti(III) and Ti(IV) in the visible region of the spectrum.

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COULOMETRIC DETERMINATION OF CHROMIUM

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INTRODUCTION

Coulometry at controlled potential is an analytical procedure in which the substance being determined is quantitatively reduced or oxidized from one oxidation state to another. This paper describes a procedure for the determination of chromium in which controlled-potential electrolyses are employed to convert chromium to the +2 state while removing or rendering innocuous a number of other elements. The quantity of electricity consumed in re-oxidizing the chromium to the +3 state in another controlled-potential electrolysis is then measured. This procedure permits the determination in pure solutions of as little as 5 μg of chromium with an accuracy and precision of ±1% or better, while 0.1 mg or more can be determined with an accuracy and precision of the order of ±0.1%. Very few other elements interfere in the final measurement.

EXPERIMENTAL

The characteristics of the potentiostat and current integrator, which were manufactured by Analytical Instruments, Inc., Bristol, Conn., have been described elsewhere[1], as has the double-diaphragm cell used. The general experimental procedure was substantially identical with that previously described[1].

The stock solution of chromium(III) employed had been prepared determinately from National Bureau of Standards potassium dichromate by reduction with hydrogen peroxide in a sulfuric acid medium. All other chemicals were ordinary reagent grade and were used without special purification. Weights and volumetric apparatus were calibrated by conventional procedures.

DATA AND DISCUSSION

Current-potential curves of chromium(III) and (II)

The rationale of the conditions selected for the necessary preliminary reduction of the chromium to the +2 state is illustrated by the current-potential curves shown in Fig. 1, which were obtained by manual manipulation of the bridge of the potentiostat. It may be noted that these curves are not exactly reproducible when secured in this fashion, for the current at any potential is partly dependent on the quantity of electricity that has been consumed up to the instant of measurement, and this in turn depends on the rate of change of the working electrode potential, which cannot be kept constant when the current-potential curve is scanned manually. Nevertheless, the general nature of the phenomena involved is easily deduced from these curves.

Curve a is the current-potential curve for a large stirred mercury working electrode in a 6*M* hydrochloric acid solution containing 14 m*M* violet chromium(III). The $[Cr(H_2O)_6]^{+3}$, which is the principal constituent of this solution, is very irreversibly reduced, as shown by the fact that its reduction "wave" overlaps the region of rapid hydrogen evolution, which begins at about —1.0 V.

The solution of curve a was electrolyzed at —1.10 V until the current had fallen to a constant value of 105 mA, and the resulting solution of chromium(II) was found to give the current-potential curve shown in curve b. In agreement with the conclusions of PECSOK AND LINGANE[2] concerning the polarography of chromous ion in concentrated chloride solutions, this curve indicates that the oxidation of chromium(II) in 6*M* hydrochloric acid proceeds reversibly at a mercury electrode. The curve further demonstrates that quantitative reoxidation of chromium(II) to the +3 state in 6*M* hydrochloric acid can be accomplished at any potential between about —0.25 and —0.45 V *vs.* S.C.E.

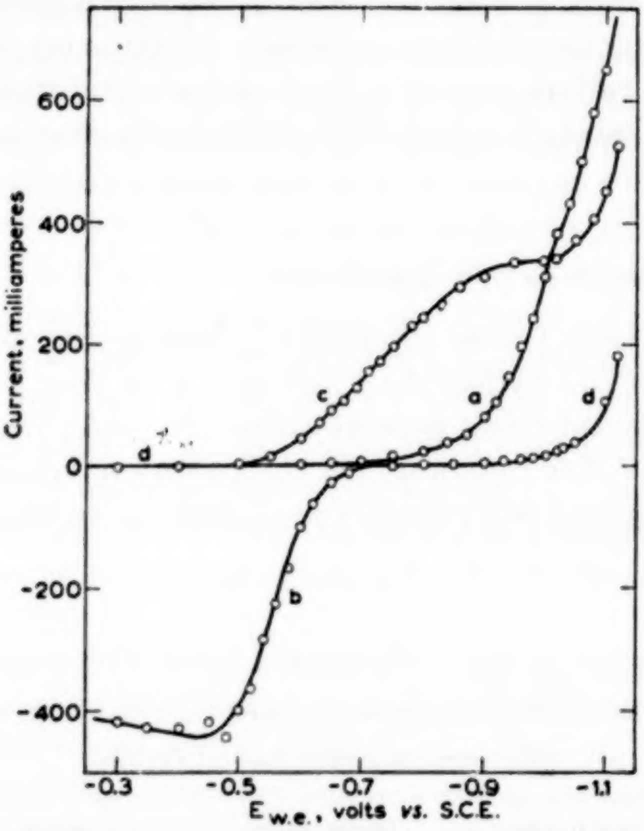

Fig. 1. Current-potential curves for a large stirred mercury working electrode in 6*M* hydrochloric acid solutions containing (a) 14 m*M* violet chromium(III); (b) 14 m*M* chromium(II), prepared by a controlled-potential electrolysis of (a) at —1.10 V *vs.* S.C.E.; (c) 14 m*M* green chromium (III), prepared by a controlled-potential oxidation of (b) at —0.40 V *vs.* S.C.E.; (d) residual current curve of 6*M* hydrochloric acid alone.

The electrolytic oxidation of chromium(II) under these conditions yields a chromium(III) solution that is green instead of violet, and which gives a current-potential curve (Fig. 1, curve c) consisting of a drawn-out wave having a fairly well-defined plateau, which begins at about —0.95 V *vs.* S.C.E. This indicates that green chromium(III) should be quantitatively reducible to the +2 state in 6*M* hydrochloric acid at any potential more negative than —0.95 V *vs.* S.C.E., a conclusion that is confirmed by coulometric analyses of solutions prepared in the manner just described. However, violet chromium(III) cannot be completely reduced unless the potential is at least as negative as —1.10 V, and, consequently, it is necessary to use a potential no less negative than this in the pre-reduction step in order to be sure that all of the chromium contained in an unknown will be reduced to the +2 state before beginning the coulometric measurement.

Similar phenomena are observed in solutions containing perchloric, phosphoric or sulfuric acids, or even hydrochloric acid at a concentration below about 5*M*; in every case a portion of the chromium(III) escapes reduction even at potentials at which hydrogen is being vigorously evolved at the working electrode. In all of these media the highly hydrolyzed species of chromium(III) are only very slowly converted into reducible forms in the bulk of the solution as the equilibria are displaced by the electrolysis. It is interesting to note that, although solutions prepared by adding violet chromium(III) to 1*M* sulfuric acid or 43% phosphoric acid appear stable indefinitely, the electrolytic oxidation of chromium(II) in these media gives insoluble green chromic sulfate or phosphate.

Determination of chromium in pure solutions

The data shown in Table I were obtained by electrolyzing solutions of violet chromium(III) in 60 ml of 6*M* hydrochloric acid at —1.10 V *vs.* S.C.E. until the current had decreased to a constant value, generally about 100 mA, then measuring the quantity of electricity required to re-oxidize the chromous ion during a further electrolysis at —0.50 V *vs.* S.C.E. As can be easily perceived from the equation given by LINGANE[3]

TABLE I

COULOMETRIC DETERMINATION OF CHROMIUM IN PURE SOLUTIONS

(See text for experimental details)

mequiv. Cr taken	*Input resistor (ohms)*	*Initial current (mA)* *	*mequiv. Cr found*	*Error (%)*
1.0064	1	**	1.0059	—0.05
(52 mg)			1.0070	+0.06
			1.0058	—0.06
			1.0060	—0.04
			1.0069	+0.05
0.20132	1	225	0.20167	+0.17
			0.20087	—0.22
			0.20116	—0.08
0.03957	10	44	0.03953	—0.10
			0.03959	+0.05
			0.03964	+0.17
0.008010	100	8.7	0.008025	+0.19
			0.008004	—0.08
0.002006	100	2.2	0.002004	—0.10
			0.002007	+0.05
0.000403	1000	0.45	0.000401	—0.5
			0.000404	+0.3
0.0001009	1000	0.11	0.000100	—0.9
			0.000102	+1.1

* Corrected for residual current (*ca.* 0.03 mA).

** >1 A.

for an electrolytic process in which E_c-E_a is negative (as is usually - though not necessarily - the case), while the working electrode is serving as the anode (so that i is also negative), the total voltage applied to the cell must change sign as the electrolysis proceeds and the current decreases. This necessitates the introduction of an external bias voltage in series with the cell so that the output voltage of the potentiostat will retain the same sign throughout the electrolysis. This is easily done by connecting the positive terminal of an ordinary 1.5-volt dry cell to the auxiliary electrode, and the other terminal to the lead from the potentiostat.

Traces of atmospheric oxygen are rapidly and completely reduced by acidic solutions of chromous ion[4], and therefore great care must be taken to remove oxygen from the stream of gas used for deaeration. In experiments similar to those reported in Table I, the average error attributable to the use of tank "prepurified" nitrogen, stated to contain no more than 0.001% oxygen, was —0.6 μequiv. of chromium. When this gas was passed through an efficient gas-washing bottle initially charged with 25 g of heavily amalgamated zinc and 175 ml of 0.1*M* chromic chloride-1*M* hydrochloric acid, and then through another similar bottle filled with water to trap droplets of chromous ion sprayed over from the first bottle, the error fell to about —0.004 μequiv. The insertion of a second chromous chloride wash bottle reduced the error still further, so that it could no longer be certainly detected even in the determination of 5 μg (0.1 μequiv.) of chromium.

These data demonstrate that 0.002 mequiv. (0.1 mg) or more of chromium can be determined with an accuracy and precision of $\pm$0.1% or better, and that even 5 μg of chromium can be determined within about $\pm$1%. The 5-μg limit is, in fact, determined by the accuracy of the correction for the residual current; in the experiments cited in the Table this averaged 30 μA, and the correction constituted over 35% of the total quantity of electricity flowing through the cell. In dealing with very small amounts of chromium, it is, of course, necessary to exercise extreme precautions against air-oxidation.

Non-interfering elements

The above procedure can be used without any modification to determine chromium in the presence of aluminum, arsenic (V) and iron(II), manganese, and the alkalies and alkaline earths. None of these is reduced from 6*M* hydrochloric acid at a mercury cathode whose potential is kept constant at —1.10 V, and none interferes even when present in very large amounts.

Antimony and arsenic(III) are reduced, to stibine and arsine, respectively, but these are volatilized into the very rapid gas stream which must be employed, and hence do not interfere. Silver, bismuth, mercury, cobalt and nickel are reduced to the metals,* but these are not re-oxidized at any potential that is sufficiently negative to prevent the anodic dissolution of mercury. As has been previously noted[5,6], nickel decreases the overpotential of hydrogen evolution on a mercury surface, but in 6*M* hydrochloric acid the effect amounts to only about 0.05 V, which is negligibly small.

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* The statement that cobalt and nickel are nearly insoluble (*ca.* 10^{-7} mole per cent) in mercury is familiar to every polarographer. It is, therefore, of interest to record the fact that an electrolytically-prepared mixture containing 0.2% of metallic cobalt or nickel by weight in mercury is, to all appearances, a perfectly clean bright amalgam.

The preliminary electrolysis at —1.10 V also serves to reduce cerium(IV)[*], iron (III)[*], and titanium(IV); the reduced states of these elements are inert to re-oxidation at —0.4 V *vs.* S.C.E.

Cadmium, copper, indium, lead, thallium, tin(II) and (IV), and zinc are reduced to their amalgams during the reduction at —1.10 V, and would be reoxidized at —0.40 V together with the chromium(II). They may be eliminated by simply draining the mercury out of the cell at the end of the reduction step, with due care to keep the electrolysis circuit connected until the last possible instant. If zinc, but no other of these elements, is present, it may be eliminated even more simply by anodic stripping at a potential of —0.80 V *vs.* S.C.E.; this quantitatively oxidizes zinc while preventing any re-oxidation of chromium.

Uranium is reduced to the +3 state at —1.10 V. Since the re-oxidation of uranium to the +4 state at —0.4 V would interfere with the determination of chromium, the uranium must be re-oxidized to the +4 state by an electrolysis at —0.80 V before proceeding to the re-oxidation of the chromium. The uranium(IV) thus produced cannot be further oxidized at a mercury cathode in strong hydrochloric acid.[8][**]

Interfering elements

Molybdenum is reduced to the +3 state at —1.10 V and is not re-oxidized electrolytically at —0.40 V. Chromium can therefore be determined without difficulty by the above procedure in the presence of no more than an equal weight of molybdenum. However, in view of the well-known ability of molybdenum(III) to catalyze the reduction of nitrate and nitrite[9], it is no surprise to find that it is also capable of catalyzing the reduction of hydrogen ion. This manifests itself by a considerable increase in current even at —0.70 V *vs.* S.C.E. on adding a trace of molybdenum to a controlled-potential electrolysis cell containing $6M$ hydrochloric acid. It is not known whether the reaction between molybdenum(III) and hydrogen ion yields molybdenum(IV) or molybdenum(V), but for present purposes the question is unimportant: whichever of these oxidation states is formed oxidizes chromous ion, and the net result is a catalysis of the reaction between chromium (II) and hydrogen ion. The error thus caused depends on the rates of the chemical reactions involved as well as on the length of time required for the electrolytic oxidation of the chromium(II). With all other factors (solution volume, temperature, stirring rate, electrode area, etc.) constant, the *absolute* error is independent of the quantity of chromium present but directly proportional to the quantity (*i.e.* concentration) of molybdenum. This is shown by Fig. 2, and it indicates not only that the reaction between molybdenum(III) and hydrogen ion is the rate-controlling step, but also that this reaction is first-order with respect to molybdenum(III). Under the conditions of these experiments the *relative* error introduced into the determination of 25 mg of chromium by the presence of 25 mg of molybdenum was barely 0.1%, but with 25 mg of chromium and 1 g of molybdenum the results were 4.1 ± 0.3% low. Once data of this sort have been secured under conditions identical in every way with those to be employed in the actual analyses, it should be possible to determine chromium with good accuracy in materials containing up to 20 or 30 times as much molybdenum by weight merely by applying an appropriate correction to the coulometric data for the amount of molybdenum known to be present.

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[*] Many experimenters have encountered difficulty in electrolyzing halide solutions containing powerful oxidizing agents with large stirred mercury electrodes. To avoid the complications that arise from the formation of mercurous chloride and the dispersal of the mercury into tiny droplets[7], it is convenient to use the following procedure. After filling the central and auxiliary electrode compartments of the cell, a suitable volume of mercury is added to the working electrode compartment. Then the solution being analyzed is added and is electrolyzed *without stirring* at a potential slightly more negative than the potential at which mercury begins to be oxidized. After most of the oxidizing agent has been reduced, the stirrer is started slowly, and gradually brought up to normal operating speed, and the electrolysis may then be continued in the ordinary fashion. As much as 5 g of ferric iron may be reduced in this way from 100 ml of $6M$ hydrochloric acid at a working electrode potential of —0.40 V *vs.* S.C.E. without the formation of any suspended mercurous chloride.

[**] Attempts were made to determine uranium by reducing it to the +3 state electrolytically, then measuring the quantity of electricity required to re-oxidize it to the +4 state. The results were about 5% low in $6M$ hydrochloric acid and 0.8% low in $0.1M$ hydrochloric acid. The error increased if the uranium(III) solution was allowed to stand, even under scrupulously deoxygenated nitrogen, before the electrolytic reoxidation was started. These facts evidently reflect a rapid oxidation of uranium(III) by hydrogen ion.

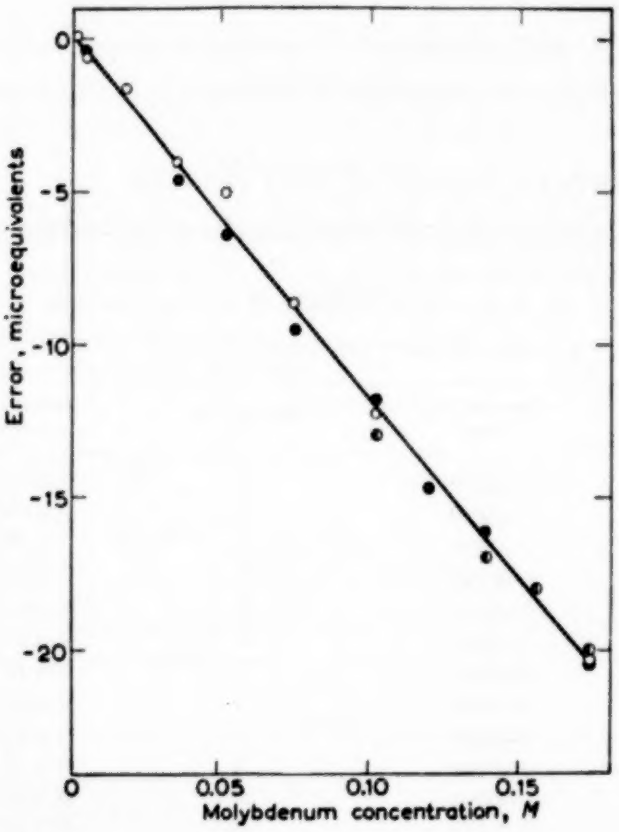

Fig. 2. The effect of molybdenum concentration on the coulometric determination of chromium. The data were secured in electrolyses of 60-ml portions of solutions containing $6M$ hydrochloric acid, known amounts of molybdenum, and either 0.12 (open circles), 0.50 (solid circles), or 2.5 (half-solid circles) mequiv. of chromium.

Vanadium is reduced to the +2 state during the electrolysis at —1.10 V. This is unaffected by a subsequent electrolysis at —0.80 V, such as is recommended for eliminating the interferences of zinc and uranium, but is quantitatively re-oxidized to the +3 state at —0.40 V. This behavior is in complete accord with the polarographic data of LINGANE[10]. The quantity of electricity measured during the final electrolysis therefore gives the sum of the numbers of millimoles of chromium and vanadium present, and an accurate correction for the vanadium is easily made if its amount is known. No conditions have yet been found under which either chromium or vana-

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dium can be determined without interference from the other by controlled-potential electrolysis at a mercury cathode.

Tungsten(VI) is quite insoluble in 6*M* hydrochloric acid, but enough remains in (or re-enters) solution to cause a perceptible consumption of electricity due to re-oxidation of +3 tungsten at −0.40 V. Consequently, tungsten schould be removed by a double dehydration with hydrochloric acid and cinchonine before proceeding to the electrolytic steps.

Selenium[11], tellurium[11], and rhenium[12,13] would be expected to interfere, but these are rarely present in significant amounts in materials being analyzed for chromium.

Determination of chromium in presence of other elements

Table II shows some data secured in determinations of known amounts of chromium

TABLE II

COULOMETRIC DETERMINATION OF CHROMIUM IN SYNTHETIC SAMPLES

Other element(s) present (g)	*mequiv. Cr taken*	*Procedure**	*mequiv. Cr found*	*Error (%)*
1.00 Al	0.4990	A	0.4993	+0.06
1.00 Sb(III)	0.4990	A	0.4989	−0.02
1.00 Sb(V)	0.4990	A	0.4987	−0.06
1.00 As(III)	0.4990	A	0.4996	+0.12
1.00 As(V)	0.4990	A	0.4991	+0.02
0.50 each Ba, Ca and Mg	0.4990	A	0.4984	−0.12
1.00 Bi	0.4990	B	0.4983	−0.14
1.00 Cd	0.4990	B	0.4989	−0.02
0.20 Ce(IV)	0.4990	A	0.4996	+0.12
1.00 Co	0.4990	A	0.4985	−0.10
1.00 Cu	0.4990	B	0.4986	−0.08
0.10 In	0.1248	B	0.1246	−0.16
1.00 Fe(II)	0.1248	A	0.1249	+0.08
1.00 Fe(III)	0.1248	A	0.1248	±0.00
0.50 Pb	0.4990	B	0.4983	−0.14
1.00 Mn	0.4990	A	0.4995	+0.10
0.25 Hg(II)	0.1248	A	0.1247	−0.08
0.025 Mo	0.4990	A	0.4986	−0.08
1.00 Mo	0.4990	A	0.4787	−4.1
1.00 Mo	0.1248	A	0.1044	−16.4
1.00 Ni	0.4990	A	0.4998	+0.16
0.50 each K, Na, NH_4	0.4990	A	0.4989	−0.02
0.005 Ag	0.4990	A	0.4987	−0.06
0.08 Tl(I)	0.1248	B	0.1245	−0.24
0.50 Sn(II)	0.1248	B	0.1250	+0.16
0.20 Sn(IV)	0.1248	B	0.1247	−0.08
0.5 Ti(IV)	0.1248	A	0.1248	±0.00
0.09 W	0.4990	A	0.5026	+0.72
0.09 W	0.4990	C	0.4988	−0.04
0.13 U	0.4990	D	0.4995	+0.10
0.65 U	0.4990	D	0.4994	+0.08
0.05075 V	0.4990	A	1.494	+200
0.05075 V	0.4990	E	0.498	−0.2
1.00 Zn	0.4990	B	0.4987	−0.06
1.00 Zn	0.4990	D	0.4988	−0.04

* A: reduction at −1.10 V, followed immediately by re-oxidation at −0.40 V.
B: as A, but with replacement of mercury after electrolysis at −1.10 V.
C: tungsten removed by dehydration with hydrochloric acid and cinchonine, then as A.
D: reduction at −1.10 V, then oxidation at −0.80 V, and finally oxidation at −0.40 V.
E: as A with correction for known vanadium content.

in the presence of a number of other elements, and Table III shows the results obtained in analyses of standard samples supplied by the National Bureau of Standards. Since none of these samples contained significant amounts of zinc or uranium, the analyses were conducted by the procedure referred to as B in Table II, and the results were corrected for the vanadium contents shown on the Bureau's certificates. In every case the coulometric results agree with the certificate values to well within the uncertainty of the latter.

TABLE III

COULOMETRIC DETERMINATION OF CHROMIUM IN NATIONAL BUREAU OF STANDARDS FERRO-ALLOYS

A 0.1- or 1-g sample was taken for each analysis and dissolved in hydrochloric acid with the addition of the least possible volume of nitric acid. After evaporating nearly to dryness twice to remove nitrate, the salts were taken up in $6M$ hydrochloric acid, transferred to a controlled-potential electrolysis cell, and treated by the procedure referred to as B in Table II.

Sample description, number and composition	*% Cr found*	*Error %*
Aluminum-base alloy 85a: 0.231% Cr; 2.5% Cu, 1.6% Mg, 0.7% Mn, 0.4% Ni, 0.2% Fe, 0.1% Si, traces Ti, Zn, Pb, Sn, Ga	0.2304	—0.26
Cr-Mo steel 72e: 0.950% Cr; 0.5% Mn, 0.3% C, 0.3% Si, 0.2% Ni, 0.2% Mo, 0.1% Cu, traces P, S, V	0.951	+0.1
Ni-Cr-Cu cast iron 115: 2.17% Cr; 15.9% Ni, 6.4% Cu, 2.4% C, 1.6% Si, 1.0% Mn, traces P, S, V, Mo, Co, Ti, As	2.181	+0.5
Ni-Cr casting alloy 161: 16.88% Cr; 64.3% Ni, 15.0% Fe, 1.6% Si, 1.3% Mn, 0.5% Co, traces C, P, S, Cu, V, Mo, N	16.86	—0.1
18 Cr-11 Ni steel (Ti-bearing) 121b: 17.69% Cr; 11.2% Ni, 1.5% Mn, 0.6% Si, 0.4% Ti, traces C, P, S, Cu, V, Mo, N	17.67	—0.1
18 Cr-9 Ni steel 101d: 18.68% Cr; 9.1% Ni, 0.7% Mn, 0.5% Si, traces C, P, S, Cu, V, Mo, Co, Sn, N	18.69	+0.05
19 Cr-9 Ni-3 Mo steel 160: 19.12% Cr; 8.9% Ni, 3.0% Mo, traces C, Mn, P, S, Si, Cu, V, Co, N	19.15	+0.16

SUMMARY

This paper describes an accurate and precise method for the determination of chromium by coulometry at controlled potential. A solution of the sample in $6M$ hydrochloric acid is electrolyzed at a large stirred mercury cathode whose potential is maintained constant at —1.10 V *vs.* S.C.E.; this reduces the chromium quantitatively to the +2 state. Copper, lead, and a number of other elements are next eliminated by simply discarding the mercury and replacing it with fresh mercury; then uranium is re-oxidized to non-interfering uranium(IV) by a second controlled-potential electrolysis at —0.80 V *vs.* S.C.E.; and finally the solution is electrolyzed at a working electrode potential of —0.40 V *vs.* S.C.E. This serves to re-oxidize the chromium quantitatively to the +3

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state, and the analysis consists of measuring the quantity of electricity consumed in this oxidation.

Of the elements commonly associated with chromium, only vanadium (and, when it is present in large amounts, molybdenum) interfere in this procedure.

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THE DETERMINATION OF ALUMINUM, NICKEL, COBALT, COPPER, AND IRON IN ALNICO

by

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INTRODUCTION

The determination of the major constituents of Alnico type magnetic materials by classical methods now in use is quite tedious. For example, the determination of nickel with dimethylglyoxime requires a double precipitation and the volumetric cobalt determination requires the time-consuming plotting of the potentiometric titration curve.

It appeared that a more simplified procedure could be developed by using an ion exchange separation and a volumetric determination of all the major constituents of Alnico.

Kraus and coworkers have determined the absorption characteristics of aluminum[1], nickel[2], cobalt[2,3], copper[2] and iron(III)[4] ions on a strongly basic anion exchange resin from hydrochloric acid solutions of various concentrations. Aluminum and nickel chlorides are not absorbed over the acid concentration range of 0 to 12*M* hydrochloric acid. Cobalt has a maximum absorption in about 9*M* hydrochloric acid and decreases to zero at about 3.5*M*. Copper(II) shows a maximum absorption at about 6*M* hydrochloric acid which decreases to zero at about 3*M*. Iron(III) has an absorption maximum at about 10*M* hydrochloric acid which decreases to zero in about 0.5*M*.

If a mixture of the five major constituents of Alnico is added in 9*M* hydrochloric acid to an anion exchange column in the chloride form, the aluminum and nickel pass through the column while the copper, cobalt and iron are absorbed on the resin. This,

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of course, is due to the presence of chloride complexes of these elements. The iron is absorbed most strongly and is at the top of the column followed by the cobalt and finally by the copper.

The aluminum and nickel cannot be separated in the column since neither are absorbed from a chloride solution. However, after a back titration of an excess of EDTA (ethylenediaminetetraacetic acid) with standard copper to determine the total equivalents of aluminum plus nickel, the EDTA can be displaced from the aluminum complex by the addition of fluoride. The EDTA released is titrated with standard copper solution and the percent of aluminum and nickel are easily calculated from the data of the two titrations.

If the solvent in the column is now changed to $4M$ hydrochloric acid, the cobalt is eluted but unfortunately the separation from copper is not very good. For this reason the copper was removed electrolytically prior to adding the sample solution to the column. The absorption of iron(III) in $4M$ hydrochloric acid is still high enough to enable the cobalt to be eluted completely while the iron moves only a short distance down the column. After the cobalt is eluted, the iron may be removed from the column with $0.5M$ hydrochloric acid.

The separation of the constituents of Alnico by ion exchange appeared feasible and the analyses of each constituent was completed volumetrically by a back titration of an excess of EDTA with a standard copper solution.

PROCEDURE

a) Separation of copper

Dissolve a one g sample in aqua regia in a 150 ml beaker and evaporate to a syrupy consistency twice to remove the nitric acid. Add 5 ml of concentrated hydrochloric acid, 50 ml of water and electrolyze at 0.5 amp with a divided cell until the copper is completely deposited. This should take about 30 min and is checked by occasionally adding a small amount of water in order to expose a new platinum surface to the solution.

A convenient divided cell may be constructed by selecting a fritted glass sealing tube which will conveniently fit inside a platinum gauze anode from commercially available electroanalysis apparatus. The glass is cut off as close to the frit as possible and the portion with the frit is inserted in the center of the platinum electrode and filled with a 10% sodium sulfate solution. Insert a platinum wire to serve as an anode and immerse the electrode assembly into the solution to be electrolyzed. Connect the gauze electrode to the negative terminal and the platinum wire to the positive terminal of a d.c. power supply capable of delivering about 25 V.

Remove the beaker from the electrode assembly and rinse the electrode with water into the beaker containing the iron, cobalt, nickel, and aluminum. Insert the electrode assembly into a 250 ml beaker containing 10 ml of buffer (20 per cent NH_4Ac) and sufficient water to cover the copper deposit. Reverse the current flow in the electrode assembly and strip the copper into the buffer solution. Add an excess of $0.01\,M$ EDTA, 4-5 drops of PAN (1-(2-pyridylazo)-2-naphthol) and back titrate with a standard copper solution.

b) Ion exchange separation

Add 3 ml of 30% hydrogen peroxide to the solution from the electrolyses and evaporate to 4-5 ml. Transfer the sample with $9M$ hydrochloric acid from a polyethylene wash bottle to an ion exchange column (1 cm diameter × 35 cm long; Dowex 1 × 4*, 100-150 mesh, chloride form) which has previously been washed with $9M$ hydrochloric acid. After all the sample has entered the resin, elute the aluminum and nickel with two column volumes of $9M$ hydrochloric acid into a 250 ml beaker. Now begin the elution of the cobalt with $4M$ hydrochloric acid. The cobalt will move down the column in a blue band and when it is within about 5 cm from the bottom of the column remove the beaker containing the aluminum and nickel and receive the cobalt in another 250 ml beaker. When the cobalt is removed from the column, elute the iron with $0.5M$ hydrochloric acid into another 250 ml beaker.

* Dow Chemical Company, Midland, Michigan.

c) Determination of nickel and aluminum

Evaporate the solution containing the nickel and aluminum to about 10 ml. Transfer the solution to a 250 ml volumetric flask and dilute to volume with water. Transfer a 25 ml aliquot to a 250 ml beaker, add 10 ml of buffer (pH 4.8) and a measured amount of EDTA sufficient to complex the aluminum and nickel and provide a small excess. Heat the solution to a boil, add 4-5 drops of PAN and back titrate the excess EDTA with $0.03M$ standard Cu solution until the indicator changes from yellow to purple. This end-point gives the sum of the nickel and aluminum.

Add one gram of ammonium fluoride to the hot solution and back titrate the EDTA released from the aluminum with the $0.03M$ standard copper solution. This end-point gives the amount of aluminum present and the nickel is calculated by difference.

d) Determination of cobalt and iron

The two solutions containing the iron and the cobalt are treated in an identical manner as follows: Evaporate the solution to about 10 ml, transfer to a 250 ml volumetric flask and dilute to volume with water. Transfer a 25 ml aliquot to a 250 ml beaker, add a 5 to 10 ml excess of standard EDTA, 10 ml of buffer (pH 4.8) and back titrate the excess EDTA with a standard copper solution using an appropriate end-point indication. The results given in Table I were obtained using an automatic titrator[5] developed in this laboratory. The titrator's operation is based on an increase in current when a platinum electrode is depolarized.

DISCUSSION

The copper separation can be accomplished by ion exchange also, however, when the nickel and aluminum are eluted with $9M$ hydrochloric acid the cobalt is more strongly absorbed than copper and as a result the copper is below the cobalt in the column. When the eluting agent is changed to $4M$ hydrochloric acid the cobalt is moved down the column faster than the copper and as a result the cobalt band must pass the copper band and leave the column before the copper reaches the bottom of the column. With very slow flow rates and judicious care in changing solvents this can be accomplished. If the sample is introduced into the column in $7M$ hydrochloric acid with all five elements present and the nickel and aluminum eluted with $7M$ hydrochloric acid, then the copper and cobalt have about the same absorption. Under these conditions a separation of the cobalt band from the copper band on elution with $4M$ hydrochloric acid is somewhat easier. However, the flow rate still must be quite slow. For this reason the copper was removed electrolytically prior to the ion exchange separation. The presence of iron in the sample necessitates the use of a divided cell for the copper deposition in order to obtain a copper deposit without the use of a depolarizer which would interfere with the subsequent column separation. With the copper removed, the separation of the four remaining elements into three groups, namely aluminum and nickel, cobalt, and iron, proceeds in a routine manner. Neither the flow rate nor the time when the elution of cobalt is started is critical.

The copper determination of course could be concluded by weighing the copper deposit. In this work the copper was stripped off the cathode and titrated complexiometrically for two reasons. (A) With the method used, no attempt is made to obtain a weighable deposit. The only criterion is that the copper deposit must stick to the electrode. As a result, a high current density may be used which will give a burnt deposit and satisfactory results for copper are still obtained. (B) With small amounts of copper, the titration is as accurate as weighing the deposit, and is more convenient with the electrode assembly used.

The determination of aluminum and nickel must be done in a hot solution. The aluminum reaction with EDTA requires that the solution be heated to a boil for a few minutes[6] and also the reaction of the aluminum EDTA complex with fluoride is rapid

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and complete in a hot solution. If the titration of the sample is begun as soon as the solution is removed from the hot plate, no reheating is necessary between the two titrations.

The determination of cobalt or iron by various techniques using EDTA has been described in many publications. All of the methods using visual indicators limit the amount of cobalt or iron which may be present[7,8]. If a visual indicator is used, an appropriate aliquot should be taken so as not to exceed the permissible concentrations of cobalt or iron.

There are, of course, many procedures available for the direct titration of aluminum, nickel, copper, cobalt, and iron with EDTA as well as other back titrations of these elements. In this work, all of the elements were determined by a back titration with a standard copper solution because it is convenient to have a single standard solution and procedure for determining a number of different elements on a routine basis and the back titration with copper is ideally suited for automatic titrations[5].

The results on the analysis of some Alnico samples are shown in Table I.

TABLE I*

Al Nominal	*Al Found*	*Ni Nominal*	*Ni Found*	*Co Nominal*	*Co Found*	*Fe Nominal*	*Fe Found*	*Cu Nominal*	*Cu Found*
8.0	8.0	15.2	15.2	21.1	21.3	52.4	52.3	3.25	3.23
	7.9		15.2		21.0		52.4		3.23
	8.1		15.2		21.1		52.4		3.26
	8.0		15.1		21.0		52.5		3.25
↓	7.9	↓	15.0	↓	21.2	↓	52.3	↓	3.26
7.0	7.1	14.8	14.8	19.8	19.8	56.5	56.4	1.2	1.21
	7.1		14.8		19.6		56.4		1.23
	7.1		14.8		19.7		56.5		1.23
↓	7.2	↓	14.8	↓	19.7	↓	56.5	↓	1.22

* Nominal values determined by classical wet analysis.

SUMMARY

A method has been developed for the determination of the major constituents of Alnico based on an anion exchange separation of the chloride complexes and the subsequent determination of aluminum, nickel, copper, cobalt and iron with EDTA. The method is more convenient than conventional classical methods.

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TRIS(*o*-HYDROXYPHENYL)PHOSPHINE OXIDE AS A COLORIMETRIC REAGENT FOR THE DETERMINATION OF FERRIC IRON

by

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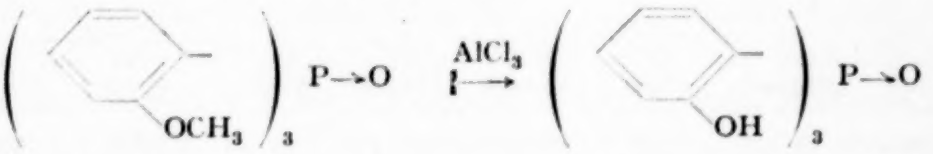
INTRODUCTION

During synthetic investigations in these laboratories for new organic chelating reagents, tris(*o*-hydroxyphenyl)phosphine oxide was successfully prepared by demethylating tris(*o*-anisyl)phosphine oxide[1] with aluminium chloride.



As the reagent showed relatively low colour sensitivity and was almost insoluble in water it was thought it would find little or no application as an analytical reagent, but further investigation showed that the reagent was almost specific for iron contained in 0.3–2.5N nitric acid solutions, and could be suitably employed as a colorimetric reagent in determining iron with other cations present, particularly the uranyl (UO$_2^{+2}$) and cupric (Cu^{+2}) ion.

The violet-red iron coloured complex was formed by adding the reagent, in ethanol, to a pipetted solution of Fe^{+3} in 0.3–2.5N nitric acid contained in a graduated flask, and then diluting the mixture with ethanol to the graduation mark. The maximum absorption of the coloured complex developed under these conditions was found to lie between 530-550 mμ. Furthermore, the colour produced closely conformed to Beer's law over a wide range of concentration (0.02–0.1 mg Fe^{+3}/ml) and remained stable for at least sixteen hours.

Although the colour sensitivity of tris(*o*-hydroxyphenyl)phosphine oxide seemed somewhat inferior to the colour sensitivity of other reagents which are more commonly employed in the colorimetric determination of iron, it was felt that the reagent did possess limited advantages over these other reagents in the working range $2 \cdot 10^2$–$1 \cdot 10^3$ p.p.m. iron, by virtue of its selectivity.

A brief literature survey revealed that 7-iodo-8-hydroxyquinoline-5-sulphonic acid[2] (Ferron) did not conform to Beer's law[3]; copper, antimony, cobalt, mercury and tin interfered in the 1:10 phenanthroline[4] estimation of iron. In the thiocyanate[5], thioglycollic[5] and *p*-aminosalicylic acid[6] colorimetric methods for estimating iron, the presence of the uranyl ion was reported to interfere; it was also reported that the silver (Ag$^+$) and mercuric (Hg^{+2}) ions seriously interfered with the 2-(2-pyridyl)-benziminazole and 2-(2-pyridyl)-iminazoline reagents[7].

Provided that the cations of metals other than iron, with the exception of the ceric

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ion (Ce^{+4}), were not present in sufficient quantity to seriously mask the colour of the iron-phosphine oxide complex, it was found that serious interference would not be encountered in iron determinations by this method. A more serious source of interference resulted from the presence, in solution, of anions other than the nitrate ion, but this has been more fully reported in a following section of this paper.

EXPERIMENTAL

Apparatus

Optical densities of the solutions were measured on a Hilger Spekker Photoelectric Absorptiometer in a 4 cm glass cell having a nominal capacity of 31 ml.

Reagent

An $0.02 M$ solution of the reagent was prepared by dissolving re-crystallised tris(*o*-hydroxyphenyl)phosphine oxide[8] m.p. 214.5-216°C in ethanol. This solution was colourless and showed negligible absorption.

Solutions

Standard solutions of different cations and anions were prepared from analytical chemical reagents.

RECOMMENDED PROCEDURE

Approximately normal solutions of nitric acid containing from 0.02–0.1 mg Fe^{+3}/ml were found to be quite suitable for determination by this method. 5 ml of such a solution was pipetted into a 50 ml graduated flask together with 5 ml reagent and the volume made up to the graduation mark with ethanol. The optical density of the violet-red solution was measured absorptiometrically and the iron content estimated by reference to the graph which had been calibrated from standard ferric nitrate solutions.

The colour reaction

(1) Effect of hydrogen ion concentration. The optical density of the solution was found to increase as the normality of the nitric acid solution was increased (Table I). The table shows that the maximum optical density was reached when the coloured complex was developed from nitric acid solutions greater than $0.3 N$.

TABLE I

Normality of 5 ml HNO_3 soln. (0.05 mg Fe^{+3}/ml) used in the determination	*Optical density*
0.016	0.43
0.0948	0.47
0.188	0.48
0.2815	0.49
0.482	0.49
1.4	0.49
2.5	0.49

(2) Maximum absorption (region). The maximum absorption of the colour in the visible region was determined in a Hilger Uvispek Photoelectric Spectrophotometer using a 4 cm glass cell (Fig. 1). The maximum absorption of the coloured complex was found to lie between 530-550 mμ, when the complex was developed from 5 ml of a $1.25 N$ nitric acid solution containing 0.05 mg Fe^{+3}/ml. Measurements were therefore made

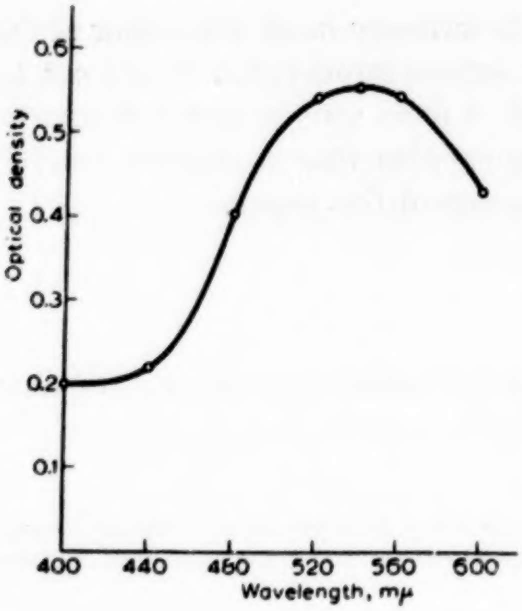

Fig. 1.

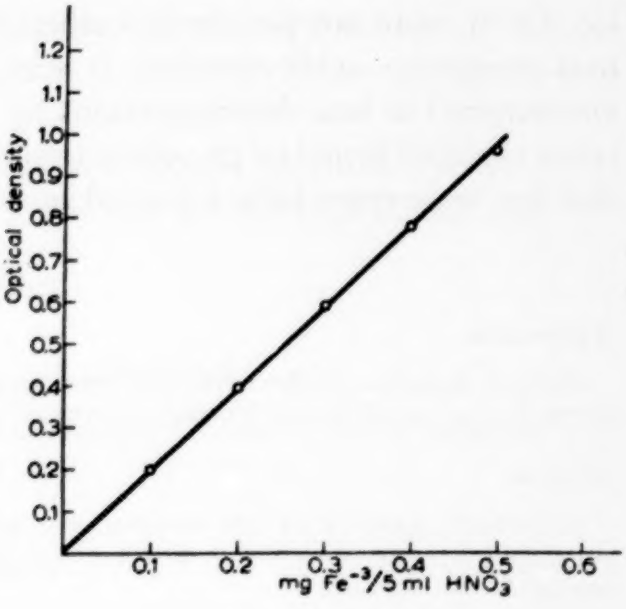

Fig. 2.

on the Hilger Spekker Photoelectric Absorptiometer using the yellow-green filter, Ilford No. 605.

(3) Stability of the colour. No change in optical density was observed after keeping a solution of the iron-phosphine oxide complex overnight.

(4) Verification of Beer's law (Fig. 2). The figure is a reproduction of the calibration graph which was used for the estimation of iron in British Chemical Standard samples, and indicated the validity of Beer's law for the coloured system.

(5) Influence of other cations. In solutions buffered at pH 5.3 tris(*o*-hydroxyphenyl) phosphine oxide was observed to form insoluble complexes with the ferric (Fe^{+3}) and uranyl (UO_2^{+2}) ion, which were respectively coloured red-brown and light beige. Standard solutions of Fe^{+3} in nitric acid were therefore spiked with varying amounts of uranyl nitrate and the optical density measured of the resulting coloured solutions (Table II).

TABLE II

mg Fe^{+3}/5 ml HNO_3	*mg UO_2^{+2}/5 ml HNO_3*	*Optical density*
0.265	0.00	0.515
0.265	0.25	0.515
0.265	0.50	0.515
0.265	0.75	0.515
0.265	2.5	0.52

None of the following cations gave a coloured solution in dilute nitric acid–ethanol mixtures with the reagent: Lithium (Li^+), sodium (Na^+), potassium (K^+), copper (Cu^{+2}), silver (Ag^+), calcium (Ca^{+2}), strontium (Sr^{+2}), barium (Ba^{+2}), magnesium (Mg^{+2}), zinc (Zn^{+2}), cadmium (Cd^{+2}), mercury (Hg^{+2}), aluminium (Al^{+3}), yttrium (Y^{+3}), lanthanum (La^{+3}), cerium (Ce^{+3}), neodymium (Nd^{+3}), samarium (Sm^{+3}), dysprosium (Dy^{+3}), zirconium (Zr^{+4}), thorium (Th^{+4}), lead (Pb^{+2}), bismuth (Bi^{+3}), chromium (Cr^{+3}), manganese (Mn^{+2}), cobalt (Co^{+2}), nickel (Ni^{+2}).

The ceric ion (Ce^{+4}), added as ceric ammonium nitrate, did however produce a brown coloration under the above conditions. Tests were, therefore, carried out to determine to what extent the ceric ion would interfere in determinations by this method (Table III).

TABLE III

mg Fe^{+3}/5 ml HNO_3	mg Ce^{+4}/5 ml HNO_3	Optical density
0.22	0.00	0.43
0.22	0.025	0.43
0.22	0.05	0.43
0.22	0.125	0.435
0.22	0.25	0.455

(6) Influence of other anions. The oxalate ion, ($C_2O_4^{-2}$) was found to interfere strongly even in very small quantities (10 p.p.m.). The effects of other anions are shown in Table IV.

TABLE IV

Anion	Added as	Interference > mg/5 ml HNO_3
F^-	NaF	0.19
Cl^-	NaCl	0.35
SO_4^{-2}	Na_2SO_4	0.96
BO_3^{-3}	$Na_2B_4O_7$	1.55
HPO_4^{-2}	Na_2HPO_4	0.24
CH_3COO^-	CH_3COONa	1.47

(7) The estimation of iron in British Chemical Standards (B.C.S.). The general procedure was to take the sample into solution with nitric acid, dilute the solution to a known volume and directly estimate the iron colorimetrically with other cations present. The phosphate anion was removed from the basic slag solution by precipitation as zirconium phosphate with a zirconium nitrate solution. The aluminium alloy was treated with sodium hydroxide solution and the undissolved material taken into solution with nitric acid for purposes of analysis.

TABLE V

B.C.S.	Iron present	Iron found
Manganese brass "B"	0.91	0.87
Basic slag "A" No. 174	8.93	8.88
Aluminium alloy No. 216	0.81	0.83

ACKNOWLEDGEMENT

Our thanks are due to Mr. G. W. C. Milner and Mr. T. H. Bates for helpful advice, also to Dr. E. S. Lane for his kind interest.

SUMMARY

Tris(*o*-hydroxyphenyl)phosphine oxide is introduced as a new colorimetric reagent for the determination of ferric iron in solutions 0.3–2.5*M* nitric acid. The only other cation known to interfere in the determination is the ceric ion (Ce^{+4}). The colour of the complex is stable and is found to obey Beer's law over a wide concentration range.

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THE CATALYTIC DETERMINATION OF MERCURY WITH POTASSIUM FERROCYANIDE AND NITROSOBENZENE

by

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INTRODUCTION

It has been known for a long time that the $[Fe(CN)_6]^{-4}$ ion may react with water to form $[Fe(CN)_5.H_2O]^{-3}$ and that the latter gives a violet complex with nitrosobenzene. The equilibrium reaction

$$[Fe(CN)_6]^{-4} + H_2O \rightleftharpoons [Fe(CN)_5.H_2O]^{-3} + CN^- \quad \ldots\ldots\ldots\ldots \quad (a)$$

is very slow, but its speed is increased by the catalytic action of mercury and by light. By addition of nitrosobenzene the very rapid reaction:

$$[Fe(CN)_5.H_2O]^{-3} + C_6H_5NO \rightarrow [Fe(CN)_5.C_6H_5NO]^{-3} + H_2O \quad \ldots\ldots \quad (b)$$

causes eqn.(a) to shift to the right. For details on the reaction mechanism and the catalytic action of mercury, the work of Asperger[1], Asperger and Parlovic[2] and Asperger, Murati and Cupahin[3], should be consulted.

Asperger and Murati[4] investigated the possibility of using this reaction for analytical purposes. They found that a relation between the extinction of the violet complex and the mercury concentration exists if the pH had a fixed value at the beginning of the reaction and if reaction time and temperature were kept constant. The relation was of the type $\log E = m \log c + k$, and the standard deviation was 9.5%.

It is strange, however, that the authors have given a fixed pH to the solution, but they have not added a buffer. Therefore, it seems possible that during the colour formation the reaction velocity changes, and that this will decrease the reproducibility of the observations. Therefore, our main purpose has been to investigate the reproducibility of this reaction when a buffer has been used. Besides, the question arose whether the standard deviation is not increased by forcing the observations to obey a mathematical relation, as was done by Asperger and Murati, since no chemical foundations for such a relation are present. This, too, was investigated.

EXPERIMENTS

Preliminary experiments with filter colorimeters with wavelength-transmittance maxima at 5000 Å (Zeiss-Pulfrich filter S 50) and 5440 Å (interference filter) showed:

(1) The pH changes with time if no buffer is used.
(2) Maximum extinction in a fixed time was obtained when buffers with pH 3.9–4.1 were used.
(3) With Hg concentrations giving an extinction of about 0.8 and more in a 4-cm cuvet, the increase of E with c was much slower than at lower concentrations.

Reagents

For the final experiments the following reagents were used:

$K_4[Fe(CN)_6]$: A $0.1M$ solution was kept in the dark. Every day 5 ml were diluted to 100 ml.

$HgCl_2$: 1 ml of a $5 \cdot 10^{-3}M$ solution was diluted every day to 100 ml, 1 ml of this final solution contained 1.00 μg of mercury.

C_6H_5NO: This was prepared according to ref.[5]; the melting point was 63°–65°C. When kept at about 0°C the solid product was stable for several months. Every day a $4.2 \cdot 10^{-3}M$ solution was prepared.

Buffers

Three buffers were used:

I. $0.025M$ citric acid } in quantities to give
$0.050M$ Na_2HPO_4 } pH = 4.09
II. $0.050M$ acetic acid } in quantities to give
$0.050M$ sodium acetate } pH = 3.90
III. The same components that were used for II were mixed in quantities to give pH = 4.1.

To a mixture of 10 ml nitrosobenzene solution, 25 ml buffer, and 0.5–7 ml $HgCl_2$ solution, distilled water is added to give 90 ml. This is placed in a thermostat of 25°C. If the mixture has the correct temperature, 10 ml of the $K_4[Fe(CN)_6]$ solution of the same temperature is added. The moment of addition is considered to be the beginning of the reaction. After 15 min, the extinction was measured at 5280 Å against a blank obtained in the same way.

The thermostat was placed in semi-darkness. As only light with a wavelength below 3500 Å influences the reaction, it will probably be possible to work with yellow or red light.

RESULTS

The results are given in columns 1, 2 and 3 of Table I.

TABLE I

THE RELATION BETWEEN THE QUANTITY OF MERCURY AND THE EXTINCTION

μg Hg	*Buffer*	*E = —logT*	*μg (calculated)*	Δ *(%)*
0.500	I	0.038	0.465	—7
	II	0.040	0.492	—2
	III	0.042	0.521	+4
1.00	I	0.075	1.02	+2
	II	0.074	1.01	+1
	III	0.073	1.00	0
2.00	I	0.134	2.01	0
	II	0.138	2.08	+4
	III	0.137	2.07	+4
3.00	I	0.193	3.08	+3
	II	0.176	2.77	—8
	II	0.184	2.92	—3
	III	0.173	2.71	—10
5.00	I	0.305	5.24	+5
	II	0.310	5.35	+7
	II	0.304	5.24	+5
	III	0.295	5.03	+1
7.00	I	0.367	6.50	—8
	II	0.394	7.08	+1
	II	0.390	6.96	—1
	III	0.376	6.68	—5

Assuming that between the quantity of mercury (c) and the extinction (E) the relation

$$\log E = m \log c + k \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad (1)$$

holds, the methods of least squares[6] gives:

$$m = \frac{n\,\Sigma(\log c \cdot \log E) - \Sigma \log c \cdot \Sigma \log E}{n\,(\Sigma \log c)^2 - (\Sigma \log c)^2} \quad \ldots \ldots \ldots \ldots \quad (2)$$

$$k = \frac{\Sigma \log c \cdot \Sigma(\log c \cdot \log E) - \Sigma \log E \cdot \Sigma(\log c)^2}{(\Sigma \log c)^2 - n\,(\Sigma \log c)^2} \quad \ldots \ldots \ldots \quad (3)$$

where n is the number of observations. Calculation gives $m = 0.859$ and $k = -1.134$. Inserting these values in eqn. (1) gives

$$\log E = 0.859 \log c - 1.134 \quad \ldots \ldots \ldots \ldots \ldots \quad (4)$$

and substituting the E values obtained into this equation gives the c values of column 4 of Table I. The deviations with column 1 are given in column 5.
The standard deviation s, is found from

$$s = \sqrt{\frac{\Sigma \triangle^2}{n-2}} \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad (5)$$

Calculation gives $s = 5\%$. If s is calculated for each of the buffers, roughly the same value is found.

The question remaining to be answered is whether the use of the relation of type 1 does not result in a larger value of s than calculation of s from the reproducibility of the parallel determinations. Therefore, $\hat{s}$, the pooled estimate of the standard deviations of the 6 series of determinations, was calculated with the formula:

$$\hat{s}^2 = \frac{\Sigma_i\,(n_i - 1)\,s_i^2}{\Sigma_i\,(n_i - 1)} \quad \ldots \ldots \ldots \ldots \ldots \quad (6)$$

where n_i is the number of determinations in the series (3 or 4) and s_i the standard deviation in each of the series[6].

The result is $\hat{s} = 3.8\%$. The F test[6] proves no significant increase in the standard deviation by use of the relation (1), and as the interpretation of results simpler by using a mathematical relation than by using a non-linear calibration curve, the use of eqn. (1) seems to have been accounted for.

It should be noted that, when strictly taken, the formulae given by YOUDEN[6] for the method of least squares are only applicable if the absolute values of the standard deviations are independent of the concentrations. In the above problem, this means that the absolute value of the deviation in log c should be constant over the whole concentration range, and, therefore, the percentage error should be constant. Table I shows no contradiction to this assumption.

References p. 383

SCOPE OF THE METHOD

(1) The concentration range may possibly be extended to lower concentrations by using a smaller volume or by increasing the reaction time.

(2) Interference is caused by Au and Pt, having a weak catalytic effect[2]. A negative salt effect is found for other elements (see Table II taken from ref.[2]).

(3) The catalytic effect of some mercury compounds deviates from $HgCl_2$[2].

TABLE II

THE INFLUENCES OF KCl ON THE EXTINCTION

KCl M	*E*
0.0	0.48
0.1	0.40
0.3	0.30
1.0	0.06

SUMMARY

Mercury can be determined in quantities of about 1 μg by catalytic effects on the decomposition of $K_4[Fe(CN)_6]$. The reaction product formed in a given period is measured colorimetrically at 5280 Å after addition of nitrosobenzene. There appears to be a linear relation between the extinction and the logarithm of the mercury concentration. As compared with the original method by ASPERGER AND MURATI the standard deviation can be reduced from 9.5 to 5.0 % by buffering the reaction mixture at an optimum pH, *i.e.* 3.9-4.1.

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Short Communication

Note on 1,2-cyclodecanedioxime

In the course of the work being done in this laboratory extending our knowledge of the dioxime analytical reagents we examined 1,2-cyclodecanedioxime. There appears to be no particular advantage of this reagent over dimethylglyoxime or nioxime but it seems desirable to record the properties of the compound briefly.

EXPERIMENTAL WORK

Synthesis of 1,2-cyclodecanedioxime. 1,2-cyclodecanedione was prepared by the method of Blomquist and Goldstein[1]. This compound was oximated in a basic water-alcohol solution in the presence of excess hydroxylamine at reflux temperature. After refluxing for one h, the solution was cooled and the dioxime was precipitated as a pink substance on acidifying the solution with acetic acid. The material was recrystallized from water, white crystals, m.p. 178-182°. Yield = 75%.

Solubility in water = 0.52 g/l at 25° corresponding to a molar concentration of 0.0026.

Nickel bis-cyclodecanedioxime. Orange yellow. Insoluble in neutral and ammoniacal solutions. Found: 12.80, 13.07, 12.94, 12.97, 12.96; averages 12.95; theoretical for Ni(cyclodecanedioxime)$_2$: 12.95.

The nickel compound can be extracted from ammoniacal solution into isoamyl alcohol, providing a colorimetric determination of nickel. The absorption spectrum of an isoamyl alcohol-ethyl alcohol solution (ethyl alcohol used to dilute the amyl alcohol extract to volume to dissolve accompanying droplets of water) exhibits two peaks, at 385 mμ and at 330 mμ. The corresponding molar extinction coefficients are 4240 and 4830, respectively. The system conforms to Beer's law up to nickel concentrations of $2.4 \cdot 10^{-4} M$.

Ferrous derivative. The ferrous ion yields red, soluble compounds with 1,2-cyclodecanedioxime in the presence of an amine. In the case of ammonia, the wave length of maximum absorption is 543 mμ; for ethylenediamine the absorption maximum occurs at 552 mμ and the molar extinction coefficient is 8080. The system conforms to Beer's law up to $10^{-4} M$ iron. The ferrous compounds are sensitive to oxygen, and sodium hydrosulfite serves to keep the iron in the ferrous state.

Palladium derivative. Palladium is precipitated quantitatively as lemon-yellow Pd(1,2-cyclodecanedioxime)$_2$ from acid solution.

Copper, bismuth and cobalt derivatives. Unlike dimethylglyoxime, 1,2-cyclodecanedioxime forms a dark brown, insoluble compound with the cupric ion. It yields with bismuth a yellow precipitate from strongly ammoniacal solution. With cobalt it forms brown soluble compounds in the presence of aromatic amines.

Summing up, 1,2-cyclodecanedioxime behaves much like dimethylglyoxime and other 1,2-dioximes in its reactions toward nickel, palladium and other metal ions.

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INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

SECTION OF ANALYTICAL CHEMISTRY
1957 REPORT

SYMPOSIA AND COLLOQUIA

At the Lisbon meeting a Symposium Subcommittee was appointed with the task to make recommendations on the holding of symposia on specific analytical subjects under the patronage of the IUPAC. There continually arises the need to collect, digest, and resolve recommendations on the holding of symposia under the patronage of the Analytical Section. There is even the greater problem of making preliminary arrangements regarding the administration of such symposia such as agreeing upon a time, place and particularly the scope of such symposia. Since it is a principal function of the Section to encourage such symposia, a subcommittee of the Section Committee was appointed (1956) to sort out the possibilities as they arise. For what seemed to be obvious reasons, the Presidents of Commissions were named with the President of the Section as an *ex officio* member.

Professor *Duyckaerts* represented the Section at the VIth Colloque International de Spectroscopie held at Amsterdam in May 1956. The VIIth Colloque is scheduled for the second week of September 1958 at the University of Liège and is being organized by the Association des Ingenieurs de l'Université de Liège. The Section approved a suggestion by Professor DUYCKAERTS that this Colloque be held under IUPAC patronage. This recommendation has obtained the approval of the Executive Committee of the Union.

Professor B. CRAWFORD, a member of the Commission on Optical Data, was appointed to represent the Section at the Ohio State Symposium on Molecular Spectra at Columbus in June 1956, which was held concurrently with the Joint Commission on Spectroscopy of the International Union of Pure and Applied Physics and the Astronomical Union. The Section approved the CRAWFORD report and was especially satisfied that there will be a close cooperation between the Commission on Molecular Spectroscopy of the Section of Physical Chemistry and our Commission on Optical Data.

During the course of the XIth Congress (1957) in Paris, a Colloquium was held (23 and 24 July) on Modern Electrochemical Methods of Analysis. This Colloquium was under the joint sponsorship of the Analytical Chemistry Section, Physical Chemistry Section and C.I.T.C.E., the meetings being held at L'Ecole Nationale Supérieure de Chimie (Paris). Introductory addresses were made by Professor T. P. HOAR (England), President of C.I.T.C.E. and Professor I. M. KOLTHOFF (U.S.A.), President of the Analytical Section, IUPAC. Professor KOLTHOFF and Professor W. KEMULA (Poland) presided at the two sessions during which 24 papers were read and discussed enthusiastically. All arrangements were made by Prof. G. CHARLOT. The Symposium was a great success.*

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* The Proceedings of this Symposium have meanwhile been published in *Anal. Chim. Acta*, 18 (1958) 1-182, and separately in book form, *Modern Electroanalytical Methods*, by Elsevier Publishing Company, Amsterdam.

RECOMMENDATIONS

In a 1949 report to Union, the need for an agreement on a standard scale of pH and for the adoption of pH standards was discussed. Two reports on this subject were made at subsequent Conferences of the Union and recently R. G. BATES (U.S.A.) and V. E. BOWER (U.S.A.) have completed work on standards for low pH and high pH, and standards for use at elevated temperatures. This matter was discussed in the Commission on Electrochemical Data and the report accepted by the Commission as being complete and correct. In presenting the matter to the Section Committee for approval, members recalled that similar work was being done in two other countries. The Commission was thereupon requested to attempt to obtain an agreement with these two bodies before presenting to the Council a recommendation on pH standards.

At the Zurich meeting a proposal by Professor P. S. TUTUNDZIC of Yugoslavia to adopt the Coulomb as standard in Volumetric Analysis was referred to the Commission on Electrochemical Data. Professor H. A. LAITINEN, Secretary of this Commission, submitted a report after consultation with internationally recognized experts in the field of coulometry. There was general agreement that the adoption of the coulomb as a standard is at least premature, because of lack of adequate data of sufficient accuracy to be comparable with the best volumetric work. As a matter of principle the adoption of a coulomb as the standard is ultimately equivalent to reference to pure silver by electrochemical rather than chemical means. At best, therefore, the coulomb could only be considered as a secondary standard. The LAITINEN report was unanimously adopted.

PUBLICATIONS

The Main Congress Lectures and Lectures in the Sections of the XVth International Congress of Pure and Applied Chemistry (on Analytical Chemistry) are available from Birkhäuser Verlag, Elizabethstrasse 19, Basel 10, Switzerland.

The Section takes great pride in announcing that Volume I of "Stability Constants of Metal-Ion Complexes with Solubility Products of Inorgauic Substances prepared by J. BJERRUM, G. SCHWARZENBACH AND L. G. SILLEN, has been published in 1957 by the Chemical Society of London, Burlington House, London, England. The publication of the Volume II by the same publisher dealing with complexity, acidity and solubility constants is planned for early 1958. These two publications, approved by the Section Committee, represent the work of the Commission on Equilibrium Data

It is also a source of great satisfaction that the "Tables on Selected Values Polarographic Data", initiated by the Commission on Electrochemical Data, have been completed by Professor G. SEMERANO AND L. GRIGGIO, the Research Center of Polarography of the Italian National Research Council, Padua. These tables have now been published by the Consiglio Nazionale delle Ricerche, Padua, Italy, as pages 247 to 562 extracted from "Contributi Teorici e Sperimentali di Polarografia", Volume 3°, Supplemento a "La Ricercia Scientifica,' (1957). These tables consist of tabulations of experimental conditions for some 315 compounds grouped as unsaturated hydrocarbons, halogen compounds, carbonyl compounds, acids and their derivatives, nitro compounds and their reduction products, sulfur compound, hetrocyclic nitrogen compounds and phosphonium salts. The tables are prepared in a uniform fashion so as to facilitate locating specific experimental conditions. These tables were approved for Union sponsorship by the Section Committee and published in 1957.

Presented to the Section Committee, and subsequently approved, were the tables on Oxidation-Reduction potentials for some 67 elements prepared by Professor G. CHARLOT, D. BÉZIER AND J. COURSIER under the initiative of the Commission on Electrochemical data. These tables, covering the literature up to 31 December, 1954, have been drawn up in order to supply the chemist with a convenient tool, so that he may find quickly the best or the most probable values of the normal oxidation-reduction potentials, or of the formal potential of a given oxidation-reduction system. These tables are complete and in manuscript cover some 200 pages (approximately 150 tables). They have been given to the IUPAC Commission on Tables des Constantes for publication (early 1959).

A Report on Inorganic Colorimetry, prepared by Professor C. DUVAL, secretary of Commission 1 on New Analytical Reagents, has been published by La Société d'Enseignement Supérieur, 5 place de la Sorbonne, Paris 5e (France) in 1956.

ADMINISTRATIVE ACTIONS

Proposed New Commission. The Commission on New Analytical Reactions and Reagents proposed that its Subcommission on Organic Functional Groups be dissolved and made into a new Commission. After extensive discussions the Section Committee at Lisbon decided that this was not an opportune time to establish a new Commission and to defer a decision until a later meeting, when more explicit conditions as to its scopes and activities could be defined. The matter is still pending.

Early in 1956 a task group, composed of ASHLEY (Chairman), FORBES, and ZACHERL, was appointed with the assignment to study the rules of the Section. This group submitted a revised set of rules which were distributed at the Lisbon meeting. Because of the absence of ASHLEY and FORBES the discussion there was only brief. At the Paris meeting the new rules were discussed in detail; and, after further extension to be made by correspondence within the Section Committee, will be submitted to the Executive Committee of the Union for approval. It was the general concensus that if the IUPAC By-Laws were more explicitly edited, there may be no need for supplementary Section By-Laws.

The Section Committee tentatively approved the following as its Scope: "Like the Union, of which it is a part, the Analytical Section in the field of analytical chemistry has as its objective the organization of permanent cooperation between the Chemical Societies of member countries, the coordination of their scientific and technical activities in this field, and assistance in the advancement of Analytical Chemistry in all its aspects, particularly by holding Meetings, Congresses, Symposia and Discussions. It does not intend to issue standard methods of analysis for any industrial purpose."

OTHER ACTIVITIES BY THE SECTION COMMITTEE

Projects of Commissions. Any new project, and its suitability for publication, must be approved by the Section prior to initiating work.

The *scope* and *activities* of Commissions will be an urgent subject of study by the Section Committee. For this purpose the Secretary, in cooperation with the Commissions, prepared a statement of Commission Scopes.

Commission presidents are *ex-officio*—non-voting—members of the Section Committee.

The Commission on Microtechniques has been inactive. The justification for continuance of the Commission will be investigated by the Section Committee.

COMMISSION ACTIVITIES

In the following a summary of the activities of various Commissions is presented.

Commission I on New Analytical Reactions and Reagents

Professor P. W. West succeeded Professor J. Gillis as Chairman in 1956. The following new Titular Members (approved of by the Section) added since 1955 as replacement for retiring members are: T. Dupuis (France), J. Hoste (Belgium), M. Ishibashi (Japan), Y. Rusconi (Switzerland), and H. Weisz (Austria). The following new Delegate member was added: N. D. Cheronis (U.S.A.). Continuing as members are: C. Duval (France-Secretary), R. Belcher (England), F. Burriel-Marti (Spain), J. H. Yoe (U.S.A.), and a Delegate, S. Veibel.

The Commission has approved the following as its Scope: "The choice and documen tation of experimentally selected and validated reactions for use in qualitative inorganic reactions".

The first report on inorganic colorimetry was issued in 1956 (see above). The fifth and sixth reports on Analytical Reactions are now in process of being prepared. It was agreed that all future work on colorimetry should be left in the hands of Commission V. The proposal to change the status of the Subcommission on Organic Functional Groups into a new Commission has been referred to above.

Commission III on Microtechniques

Prof. M. K. Zacherl (Austria) continues as Chairman; continuing as titular members are H. Malissa (Federal Republic of Germany-Secretary), R. Belcher (England), A. A. Benedetti-Pichler (U.S.A.), J. A. Kuck (U.S.A.), D. Monnier (Switzerland) and C. L. Wilson (Northern Ireland). The Subcommittee for the standardization of microchemical apparatus and equipment was dissolved pending more complete standardization in the various countries.

The Commission has approved the following as its Scope:

"Prepassing and issuing standards and recommending usages in the whole field of microchemistry".

The symbols used in the international literature for the description of the properties of precision balances are just as non-uniform as the terminology used for precision weighings. The Commission has, therefore, assumed the task to advocate recommendations for a uniform terminology along with the corresponding definitions in the English, French, and German languages. The proposals received for this purpose were up for discussion, although they differ somewhat from the terminology presented by the British Standards Institution. The Commission asked C. L. Wilson and A. Benedetti-Pichler to gather the available material and to work out suitable proposals for the systematization of the terminology. These proposals will again be discussed, and if possible, definitely settled, at the next meeting of the Commission.

A proposal on nomenclature and symbols concerning the classification of masses and weights and their abbreviations has been drafted and approved by the Commission.

These recommendations will be submitted to Commission IV for coordination with other bodies acting in this field.

Commission IV on Terminology and Expression of Results

Mr. L. W. CODD succeeded Professor R. J. FORBES as Chairman in 1956. The following new Titular Members (approved of by the Section) added since 1955 are: F. BURRIEL-MARTI (Spain), H. MALISSA (Federal Republic of Germany), L. C. MACMAHON (England); W. J. YOUDEN (U.S.A.). Continuing as members are: A. H. DODD (England), R. GAUGUIN (France), P. ROCQUET (France) and G. T. WERNIMONT (U.S.A.).

The Commission has approved the following as its Scope: "To consider, with due thought to common usage in the principal scientific languages, and to issue recommendations on format of analytical methods, on symbols, abbreviations and units for presentation of data, on terms and symbols for describing precision of results, on planning inter-laboratory test programs, and on definitions".

A concise and explicit recommended format for industrial standardized methods to provide a uniform order to the description of details has been prepared. A table of recommended symbols, abbreviations and units for the presentation and tabulation of analytical chemical data has been drafted. It is planned to coordinate both sets of recommendations with similar publications by ISO TC/47 and 12, respectively.

A list of recommended concepts, terms and symbols for use in describing precision and accuracy has been prepared. This is being coordinated with the work of ISO TC/47.

Attention has also been given to the terms and definitions used in connection with sampling. There appears to be a need for international agreement on the precise equivalents of many of these terms and a glossary in English, French, Spanish and German is being prepared for publication soon.

Contact on terminology is being maintained with the Terminology Commission of the Physical Chemistry Section (CHRISTIANSEN) and also with other Commissions of the Analytical Section.

Commission V on Optical Data

Professor G. V. M. DUYCKAERTS continues as Chairman. The following new Titular Member (approved by the Section) added since 1955 is: H. KAISER (Federal Republic of Germany). The new delegate member is: E. LOEUILLE (France). Continuing as members are W. R. BRODE (U.S.A.), B. CRAWFORD (U.S.A.), R. GAUGUIN (France), J. HOSTE (Belgium), J. LECOMTE (France), M. G. MELLON (U.S.A.), and A. C. MENZIES (U.K.). Both KAISER and LOEUILLE represent the Colloque International de Spectroscopie on the Commission.

The Commission has approved the following as its Scope: "Compilation and selection of useful data for analytical operations in the optical field".

Reports by Professors DUYCKAERTS recommended specifically that (a) Commission V on Optical Data serve as the liason between the Section of Analytical Chemistry of the IUPAC and the CSI; (b) two members of the CSI represent this Committee in the Commission Optical Data; and (c) these two members represent the CSI in questions of international character such as coordination of spectroscopic meetings, nomenclature, symbols, standardization, publication of tables of spectroscopic data, *etc.* The DUYCKAERTS' report and its recommendations were approved of by the Section Committee. The actions have been put into effect by the Commission.

Several members of the Commission have contributed to the preparation of a selection of visible and ultraviolet spectrophotometric data for organo-metallic compounds employed in analytical chemistry. The work actually finished comprises 245 pages and 230 figures. Thanks to the help of new collaborators (BELCHER, BEAMISH, CLOEYS, DUVAL, RAY) this work will be practically finished during the course of the year 1958 and a volume for publication will be presented.

The Commission is also actively engrossed with questions of nomenclature, symbols of units used in spectrophotometry, and recommendations concerning the experimental conditions that must be obtained for the measurements of optical quantities. A preliminary report on these questions has been prepared under the editorship of Dr. MENZIES, and has been discussed during the Paris meeting.

Different suggestions have been made concerning this report on the methods to be used for the standardization of visible and ultraviolet spectrophotometers according to wave lengths and intensity.

The Commission notes with pleasure the initiative of German chemists to organize a symposium on the occasion of the 100th anniversary of the use of analysis by spectroscopy by BUNSEN AND KIRCHNER.

Commission VI on Electrochemical Data

Dr. R. G. BATES continues as Chairman. The following new Titular Members (approved of by the Section) added since 1955 to replace retiring members are: J. COURSIER (France), P. DELAHAY (U.S.A.), and N. TANAKA (Japan). The following new National Representatives are: M. ISHIBASHI (Japan), W. Kemula (Poland), and J. PROSZT (Hungary). Continuing as members are H. A. LAITINEN (U.S.A., Secretary), G. CHARLOT (France), J. HEYROVSKY (Czechoslovakia), G. KORTÜM (Federal Republic of Germany), and G. SEMERANO (Italy).

The Commission has approved the following as its Scope: "Formulating conventions and furthering decisions necessary to achieve increased accuracy in electrochemical analysis and a high degree of uniformity in the collection and tabulation of electrochemical data; the compilation and dissemination of selected electrochemical data of analytical importance".

The activity of the Commission on Electrochemical Data during the past two years has centered on the compilation of three types of data. The collection of polarographic data, carried out under the direction of Professor SEMERANO, has led to the publication in early 1957 of the volume described above. A manuscript of selected Oxidation-Reduction potentials, prepared under the supervision of Professor CHARLOT, was presented at Paris and approved by the Commission and by the Analytical Section; this valuable work described above will be published by Tables de Constantes early in 1958 as described above. A third compilation, a critical collection of dissociation constants for acids and bases, is progressing under the direction of Professor KORTÜM and will probably be completed in 1959.

Prof. KORTÜM reported that his critical tabulation of the data on the dissociation constants of weak electrolytes now comprises about 200 acids. Also completed is a critical analysis and discussion of the errors and possibilities of the three most important methods of determining dissociation constants, namely spectrophotometry, potentiometry, and conductometry. The constants for the aliphatic monocarboxylic acids have been completed, and considerable progress has been made on the aliphatic dicarboxylic acids, the halogen-substituted fatty acids, the mono-substituted benzoic acids, and the saturated cyclic carboxylic acids.

A new project, the critical examination of the nomenclature and terminology of electroanalysis, has been initiated under the supervision of Professor DELAHAY and has been approved by the Section Committee.

A proposal by Prof. P. S. TUTUNDZIC (*Anal. Chim. Acta*, 8 (1953) 182) that the IUPAC recommend the adoption of the coulomb as a primary standard in volumetric analysis has been referred to the Commission for study. An outline of the proposal and documentation pertaining to it was distributed to 50 electroanalytical chemists in 11 countries for comment. The opinions expressed in the 26 replies formed the basis of a report prepared by Prof. H. A. LAITINEN, Secretary of the Commission. The report, which recommended that the proposal be disapproved, was accepted by vote of the Commission (and by the Section, see above).

Commission VII on Equilibrium Data

Professor L. G. SILLEN continues as Chairman. The following new Titular Members (approved by the Section) added since 1955 are: J. C. HINDMAN (U S A.), D. N. HUME (U.S.A.). The following new Delegate member was added: T. TAKAHASHI (Japan). Continuing as members are: J. BJERRUM (Denmark), W. FEITKNECHT (Switzerland), H. M. N. H. IRVING (England), I. LEDEN (Sweden), A. E. MARTELL (U.S.A.), A RINGBOM (Finland) and G. SCHWARZENBACH (Switzerland).

The Commission has approved the following as its scope: "(a) The compilation of data on complexity constants; since this is a new field, it seems preferable to make a comprehensive rather than a critical compilation; (b) the compilation of solubility data; will concentrate on sparingly soluble substances (in general with an inorganic cation), the solubilities of which have, or may have, analytical importance".

As mentioned above the monumental tables on equilibrium constants are being published by the Chemical Society of London. These were collected in three sets: from Copenhagen (J. BJERRUM and coworkers, on both inorganic and organic ligands), from Zürich (G. SCHWARZENBACH and coworkers, on organic ligands), and from Stockholm (L. G. SILLEN and coworkers, on OH^- and halide complexes). Volume I dealing with organic ligands has already been published (1957) and the first drafts of Volume II dealing with inorganic ligands have been sent to the printer. After a number of years, supplementary tables to the above (or new editions) will become desirable. To facilitate these, card files on new work will be kept: for organic ligands by G. SCHWARZENBACH (and independently by A. MARTELL) and for inorganic ligands by L. G. SILLEN. Both undertook to let the Commission know if they were to cease this work.

The Commission greeted with enthusiasm the willingness of W. FEITKNECHT to work out a comprehensive and really critical discussion of the solubilities of hydroxides. Such a work by this expert would be a very valuable contribution to chemical literature, and it was considered probable that means for its publication could be obtained in one way or another. It was, however, understood that a critical review along the same lines for all solubility data, although desirable would not be possible at present, especially for financial reasons.

Respectfully submitted,

Minneapolis, August 1957

I. M. KOLTHOFF

BOOK REVIEWS

Oxine and its Derivatives by R. G. W. HOLLINGSHEAD, Butterworhts Scientific Publications, London Vols. I and II, pp x + 616, 1954, Vols. III and IV, pp 617-1211, 1956, £ 2,2,— per volume.

The first two volumes of this text appeared three years ago, but it is only now possible, with the publication of the last two volumes, to judge this vast work as a whole. The author has collected in these four volumes virtually everything that has ever been written about oxine (8-hydroxyquinoline) and its derivatives.

Volumes I and II cover the preparation, properties and uses of oxine itself. The greatest part deals with the analytical applications of oxine but its biological and other uses are also considered. The analytical reactions of twenty-six metals or groups of metals with oxine, as well as the determination of silicate and phosphate as the complex molybdate salts, are described in detail; information is also given on the oxinates of several metals of lesser importance. Appendices conveniently tabulate absorption maxima, drying temperatures and pH ranges for precipitation and extraction.

Volumes III and IV cover the derivatives of oxine. These are classified as the Salts of Oxine, and the Mono-Halogen, Di- and Tri-Halogen, Methyl, Sulphonic Acid, Carboxylic Acid, Phenyl and Substituted Phenyl, Nitroso, Nitro and Amino, Azo, Hydroxy, and Miscellaneous Derivatives of Oxine. The antibacterial and antifungal action of oxine is dealt with in the last chapter. Finally, an addendum of about 150 pages brings the whole literature up to date to 1956.

The author has presented all the available material but has not attempted to be critical. His choice is very wise, for too many authors aspire to make a critical survey of material which they only understand in part. And to give authoritative judgement on the many conflicting statements in these volumes would require a lifetime's devotion to practical research. Considering the vast literature which has been abstracted and the many translations required, there appear to be very few errors; and Mr. HOLLINGSHEAD is to be congratulated on the clarity of his presentation.

From the viewpoint of the analytical chemist, the results of research on oxine derivatives are disappointing. No other reagent has been subjected to the same exhaustive studies as regards the preparation of derivatives and the determination of the physical constants of the derivatives and their metal complexes. A great deal of interesting information has thus been gathered, but none of it has led to the development of an outstanding reagent; much more data on the effect of structure must be obtained before it will become possible to design reagents for specific uses. Up to the present time, the few derivatives of oxine which are of analytical value have been found more by an empirical approach to the problem than by an extensive study of structural relationships.

For the analytical chemist who is not specially interested in oxine chemistry as such, the first two volumes have by far the greater value. The whole series will save its reader endless hours of literature research; and, most important, the reader can be reasonably sure that the whole literature has been covered. These volumes should find their place on every reference shelf.

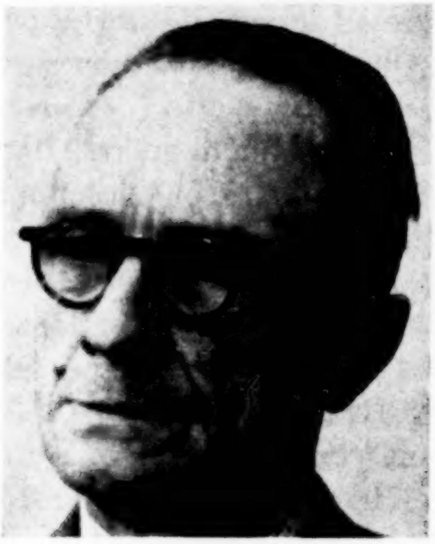
A. M. G. MACDONALD (Birmingham)

Organische Fällungsmittel in der quantitativen Analyse, von W. Prodinger, Ferdinand Enke Verlag, Stuttgart, 4. Aufl., 1957, xv + 246 Seiten, Geheftet DM 33.—. Ganzleinen DM 35.60.

Eine Zusammenstellung von der Art, wie sie hier vorliegt, kommt sicher den Bedürfnissen des analytisch arbeitenden Chemikers entgegen. Dies zeigt sich schon darin, dass drei Jahre nach Erscheinen der 3. Auflage nunmehr die 4. Auflage dieses Buches vorliegt. Von den verschiedenen Substanzen, die seither als organische Fällungsmittel vorgeschlagen wurden, ist keine bei der Neubearbeitung aufgenommen worden. Solange sich nicht absehen lässt, welche dieser Substanzen mehr als theoretische Bedeutung erlangen wird, ist das immerhin berechtigt. Arbeiten, die zu den bereits früher besprochenen Reagentien in der Zwischenzeit erschienen sind, (in erster Linie zum Natriumtetraphenyloborat, ferner zum 8-Hydroxychinolin, Cupferron, zur Mandelsäure und zum Triphenylzinnchlorid) wurden weitgehend berücksichtigt, wodurch der Umfang des Buches um etwa 5% zugenommen hat. Der Charakter des Buches ist dadurch in keiner Weise geändert worden, zumal im Übrigen der Text der 3. Auflage durchwegs wörtlich übernommen worden ist. Aus diesem Grunde darf bezüglich einer allgemeinen Wertung des Werkes auf die Besprechungen jener Auflage hingewiesen werden.

H. BODE (Hannover)

PAUL-E. WENGER
70 ANS



PAUL-E. WENGER est né à Genève, le 27 avril 1888. Il fait ses études dans sa ville natale, où se déroule également toute sa carrière scientifique. Entré à l'Université en 1906, il acquiert le doctorat ès Sciences physiques en 1911. Après avoir été chef de travaux du Professeur L. **DUPARC**, il est nommé professeur extraordinaire en 1918 et, en 1933, professeur ordinaire de chimie analytique à la Faculté des Sciences et directeur de l'Institut de Chimie Analytique et de Microchimie de l'Université de Genève. Il est doyen de la Faculté des Sciences de 1946 à 1954.

Après un début de carrière consacré à l'étude de nouvelles méthodes de séparation des corps dans le domaine de la chimie analytique classique, il travaille plusieurs années à l'étude d'un procédé de synthèse de l'ammoniaque.

Sa carrière prend une nouvelle orientation en 1930. Il installe à Genève un laboratoire de microchimie parfaitement équipé. C'est là, qu'avec ses collaborateurs, il effectue un travail extrêmement fécond: il applique les méthodes microchimiques non seulement au domaine analytique, mais à celui de la biologie. Il étudie l'application des réactifs organiques à la micro-, puis à la macro-analyse. Il développe une nouvelle méthode semiquantitative, permettant une rapide détermination de faibles quantités de certains métaux.

En 1934, le Congrès de l'Union Internationale de Chimie Pure et Appliquée, siégeant à Madrid, avait créé le ,,Comité International des Réactions et Réactifs Analytiques Nouveaux", qui publia un ,,Premier Rapport" en 1938. C'était davantage une compilation qu'un travail critique. De nouveaux rapports devaient paraître tous les deux ou trois ans. La guerre survint et le Comité du début fut dissous et remplacé par une commission de trois membres dont faisait partie **PAUL-E. WENGER** (avec J. **GILLIS** et C. J. **VAN NIEUWENBURG**). Le ,,Deuxième Rapport" parut à Bâle en 1945. Il est en grande partie l'œuvre du Laboratoire de Chimie Analytique de l'Université de Genève, dirigé par le Professeur **WENGER**. Les réactifs sont soumis à une critique sévère, cinq au maximum sont recommandés pour chaque élément, avec des données pertinentes concernant leur sensibilité, leur sélectivité, etc. (collaborateurs: R. DUCKERT et Y. RUSCONI). Le „Troisième Rapport" qui fait suite au premier comme travail de compilation fut publié avec la participation de PAUL-E. WENGER, en 1948. Le „Quatrième" et dernier sortit à Paris en 1950. Il succède au „Deuxième", et le choix des réactifs s'effectue sous la responsabilité du Professeur WENGER.

A la fin de la guerre, PAUL-E. WENGER équipe de nouveaux locaux où l'application des méthodes physicochimiques (potentiométrie, polarographie, colorimétrie, spectrographie) à l'analyse lui permettent de mettre en évidence le processus de certaines réactions et le comportement de certains réactifs.

Plus de 150 publications sont sorties du Laboratoire du Professeur WENGER. Outre les rapports mentionnés plus haut, il a publié avec ses collaborateurs G. GUTZEIT, R. DUCKERT, Mlle RUSCONI et D. MONNIER plusieurs manuels et traités de chimie analytique, à l'usage des étudiants et des chimistes analystes.

Membre du Comité de Rédaction de *Mikrochimica Acta* et de *Mikrochemie*, il fonde ensuite la revue ANALYTICA CHIMICA ACTA, dont il est rédacteur en chef depuis 1946.

Connu dans le monde scientifique, il est appelé à donner des conférences et des cours en France, en Belgique, en Hollande, en Yougoslavie, en Autriche et au Brésil.

Recteur de l'Université de Genève, depuis 1956, il participe aux jubilés des universités de Caen et de Fribourg-en-Brisgau en 1957. En 1958, il fait un court voyage d'études aux Etats-Unis et au Canada.

Détenteur de la médaille Lavoisier, chevalier de la Légion d'Honneur, docteur „honoris Causa" de l'Université de Sao Paulo au Brésil, il participe à la vie scientifique suisse et internationale, comme membre de nombreuses sociétés et de nombreux comités.

CORRELATION OF PHYSICAL CONSTANTS AND CHEMICAL STRUCTURE

GRAPHICAL STATISTICAL METHODS FOR THE IDENTIFICATION OF MINERAL OILS, GLASS, SILICONES, FATTY OILS, AND CATALYSTS

by

H. I. WATERMAN

with the collaboration of

C. BOELHOUWER AND J. CORNELISSEN

Technological University of Delft (The Netherlands)

I. INTRODUCTION

In modern chemical technology we often have to deal with complicated mixtures. In these cases the application of chemical analytical methods is not sufficient to obtain the necessary information for satisfactory scientific research, process development and process management. Reliable chemical methods for a detailed analysis of complicated mixtures are not available. Therefore their chemical structure will remain unknown if we restrict ourselves to the application of chemical methods only.

The ultimate analysis of a mixture of organic compounds, however important it may be, is not decisive for its structural identification; likewise, knowledge of the elementary composition of an alloy is not sufficient to describe its physical and mechanical behaviour, because the nature and phase composition of the alloy are left undetermined. The properties of silicates, *e.g.* glass, may be greatly influenced by thermal treatment while the chemical composition of the products remains unaltered.

Therefore *physical* methods of analysis have been introduced into nearly every field of scientific research, especially those methods that can be applied with accuracy. Relationships exist not only between the physical constants (and functions thereof) and the chemical structure and elementary composition, but also mutually between a wide variety of physical (and mechanical) constants. This is of value for the knowledge of several important technical properties.

The various physical constants and functions are used for the identification of complex mixtures such as mineral oils, fatty oils, plastics, resins and silicates. Separation of these products into individual components is generally impossible, and methods had to be developed in which certain structural groupings of the mixtures are considered instead of individual molecules or atoms. To identify such complicated mixtures physical constants could be applied successfully for their "structural group" analysis and for the prediction of various important technical properties.

The methods discussed have been called "Graphical Statistical Methods" since:

1. *Graphs* are generally used, for example for the correlation of physical constants of mixtures, for the structural analysis of mixtures and for graphic recording of hydrogenation, polymerization and isomerization processes.

2. For the construction of these graphs use has to be made of data of many mixtures. Therefore the data have to be treated *statistically*.

3. The mixtures investigated contain many different structural units (for example molecules), which represent a *statistical* distribution.

The development of reliable methods for structural analysis of mixtures is very laborious. Physical data of pure compounds may serve as a base for the investigations. It has, however, been proved that not in all cases can these data be simply correlated with those of the mixtures. Thus correlations of physical data of pure, individual hydrocarbons often prove not to be valid in the analysis of mineral oils. In this case physical constants of mineral oil fractions of widely different origin form a more reliable basis for the structural analysis, provided that their structure has been determined by absolute methods.

When determining the composition of mixtures it is advisable to start with the most simple case. Thus the development of methods for the structural analysis of mineral oil fractions was greatly facilitated by analytical hydrogenation, the aromatic rings being quantitatively transformed into the corresponding naphthenes. The problem is then limited to the determination of only naphthenic and alkyl carbon atoms in these saturated mixtures by means of physical constants. After this problem had been solved the analysis of *non-hydrogenated* aromatic fractions could be carried out by considering the influence of aromatics on the correlations found for the *hydrogenated* fractions; along these lines it was possible to extend the analysis step by step to more complex mixtures.

In the analysis of fatty oils complete expelling of the oxygen by a catalytic high pressure hydrogenation process reduces the problem to the analysis of saturated hydrocarbon mixtures. Such drastic chemical transformations should be executed under strongly controlled conditions only.

In principle any physical constant may be useful for structural analysis of mixtures. For practical reasons those constants should be applied that can be easily determined. High demands should be made upon the accuracy of the determinations. For example the physical constants density, refractive index, kinematic viscosity, ultrasonic sound velocity and surface tension may be chosen. Combination of constants, *e.g.* in certain "additive" functions, is useful only when the constants in question have been determined with comparable accuracy. In this respect density and refractive index may be combined, whereas molecular weight, the determination of which is not so precise, cannot always be combined with refractive index and density.

In general more independent physical constants that are sensitive to structure are needed when it is necessary to know more structural elements of a mixture. It will be clear that, dependent on the collected basic data, statistical methods for the analysis of mixtures in general only give a certain approach to their structures, but should never be considered as the ultimate purpose. Improvement of existing methods is imperative when new and more accurate data become available; the development of various physical separation methods (distillation, chromatography, thermodiffusion, etc.) and of independent physical identification methods (ultraviolet and infrared spectra, mass spectrometry) may also contribute considerably to their perfection.

It is to be expected that complete knowledge of the structure of mixtures of complicated nature will remain illusory. Nevertheless, it will be proved that it is already possible in such a case to predict physical constants from other physical constants, or functions thereof, with the same accuracy as the experimental accuracy.

There is another group of mixtures, which are too complicated to be described by a restricted number of physical constants. To this group belong many *catalysts*, namely the heterogeneous ones. Although several methods of measuring physical properties have been proposed (determination of internal surface, pore volume and pore size, X-ray diagrams), these are not sufficient to characterize their catalytic properties, *viz.* their activity in influencing chemical transformations, even in more simple reactions. It has been proved, however, that also for these complex mixtures characterization is possible by means of a certain limited number of *parameters* that can be determined by a simple method of graphic tracing. This principle has been applied to a large number of complex catalytic reactions and offers the possibility of a direct comparison of catalysts in all kinds of chemical transformations under different reaction conditions.

This shows the many-sidedness of the principles that are developed in the following pages.

II. MINERAL OILS AND RELATED HYDROCARBON MIXTURES

1. INTRODUCTION AND DEFINITIONS

Mineral oils consist chiefly of mixtures of hydrocarbons, besides sulphur-, nitrogen- and oxygen-containing compounds in varying quantities. The number of constituents is generally too large to make possible the separation of the individual compounds from the oils or oil fractions. Thus it is not possible to analyse mineral oils according to quantity and character of the separate hydrocarbons, or S-, O-, and N-containing compounds.

A solution to the problem of determining the composition of mineral oil fractions, especially those of high molecular weight, is provided by dealing with the oil fractions in a statistical way, *i.e.* some characteristic structural elements in the mixture are defined and determined by appropriate means.

In this monograph only those mineral oils are discussed that have a molecular weight higher than 200, that do not contain compounds with olefinic double bonds (as is the case, for instance, with several cracked products), and that do not contain compounds with oxygen or nitrogen in the molecules. Olefins are generally present in only very small amounts in mineral oils. It should be mentioned here that the hydrogen value, introduced by VAN WESTEN for the determination of the olefinic non-saturation, has recently been improved and simplified by SIE AND WATERMAN[1]. Ozonization techniques also have been brought to perfection; in this connection the work of BOER AND KOOYMAN[2] should be consulted.

The following structural elements will be determined: ring-number per average molecule* in naphthenic structure ($= R_N$), ring-number per average molecule in aromatic structure ($= R_A$), total ring-number per average molecule ($= R_T$ being equal to $R_A + R_N$), the percentage of carbon atoms (of the total number of carbon atoms) present in naphthenic structure (= $\%C_N$), the percentage of carbon atoms present in aromatic structure (= $\%C_A$), the percentage of carbon atoms present in ring structure (= $\%C_R$ being equal to $\%C_A + \%C_N$) and the percentage of carbon atoms present in paraffinic structure (= $\%C_P$), while $\%C_A + \%C_N + \%C_P = 100$. Thus in the compound

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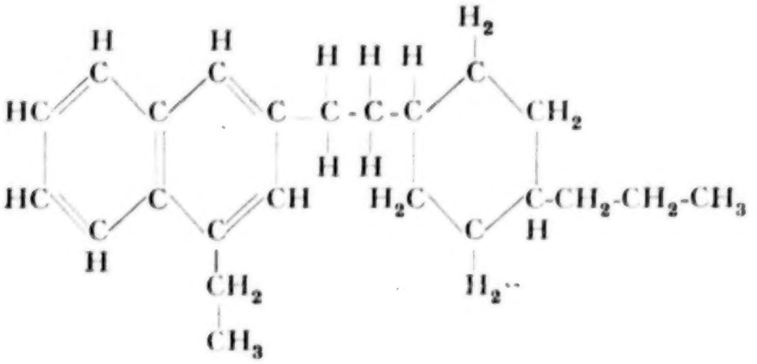
* A hypothetical molecule which represents the average nature of the molecules present in the mixture.



$R_A = 2$

$R_N = 1$

$R_T = 3$

$\%C_A = 43.5$

$\%C_N = 26.1$

$\%C_P = 30.4$

Another important structural element is the degree of branching of the mixture. The definition and a description of its determination will be given in section II 4 (p. 451).

More detailed knowledge of the composition of mineral oils can be obtained by splitting the oils into as narrow fractions as possible by means of fractionation, thermodiffusion, chromatography, extraction and other means. On the opposite page a scheme is given as an illustration of the application of distillation techniques in the investigation of mineral oils and polymerized fatty oils.

Spectrographic data are gradually becoming more important for the analysis of hydrocarbon mixtures. These methods will not be discussed as they fall outside the scope of this monograph.

2. RING ANALYSIS AND CARBON-TYPE ANALYSIS OF MINERAL OIL FRACTIONS

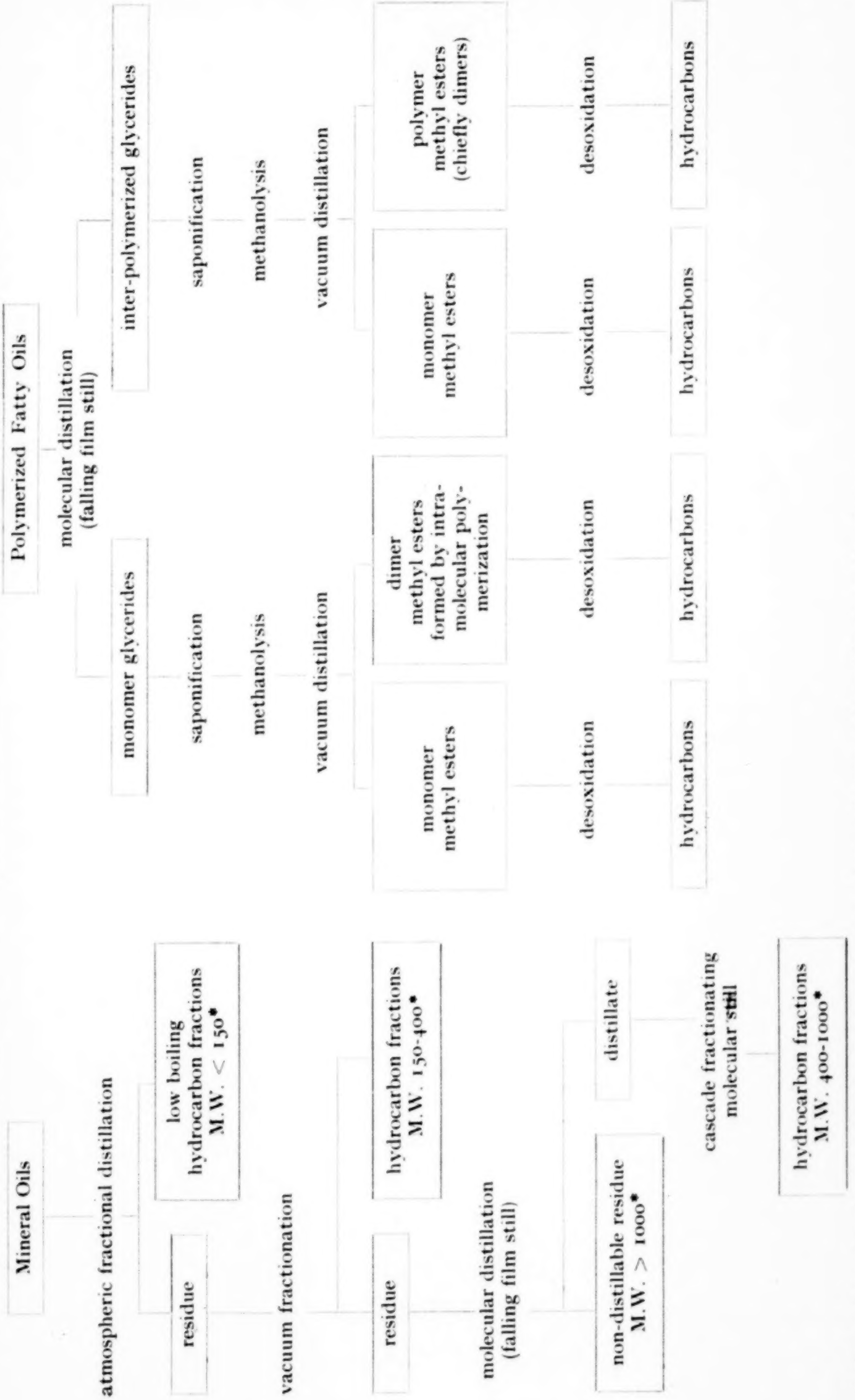
a. Analytical hydrogenation of mineral oils

When determining the composition of mixtures it is advisable to start with the most simple case. In the field of hydrocarbon mixtures this means the investigation of saturated fractions, obtained by careful hydrogenation of aromatic-containing fractions. Hydrogenation is carried out by means of a selective, catalytic hydrogenation process, which consists of treating the fraction with hydrogen at high pressure (up to 200 atmospheres) and high temperature (up to 300°C) in the presence of nickel on kieselguhr for a period that is dependent on the structure of the oil.

Especially when larger amounts of foreign elements (sulphur, nitrogen, oxygen) are present, precautions are necessary to avoid undesired side reactions, such as cracking, ring opening or ring formation, during the hydrogenation process. VAN NES AND VAN WESTEN[3] described a stepwise hydrogenation technique: in a prehydrogenation procedure mainly the elimination of the foreign elements was achieved; the actual saturation of the aromatics followed in a second step. Details are given in their book[3].

When highly aromatic fractions are hydrogenated prolonged heating of the completely hydrogenated material in the presence of nickel catalyst and high pressure

APPLICATION OF DISTILLATION TECHNIQUES IN THE INVESTIGATION OF MINERAL OILS AND POLYMERIZED FATTY OILS


Mineral Oils
atmospheric fractional distillation
residue
low boiling hydrocarbon fractions M.W. < 150*
vacuum fractionation
residue
hydrocarbon fractions M.W. 150-400*
molecular distillation (falling film still)
non-distillable residue M.W. > 1000*
distillate
cascade fractionating molecular still
hydrocarbon fractions M.W. 400-1000*
Polymerized Fatty Oils
molecular distillation (falling film still)
monomer glycerides
inter-polymerized glycerides
saponification
saponification
methanolysis
methanolysis
vacuum distillation
vacuum distillation
monomer methyl esters
dimer methyl esters formed by intra-molecular polymerization
monomer methyl esters
polymer methyl esters (chiefly dimers)
desoxidation
desoxidation
desoxidation
desoxidation
hydrocarbons
hydrocarbons
hydrocarbons
hydrocarbons

* The indicated molecular weights are approximate values and serve only to illustrate the scheme.

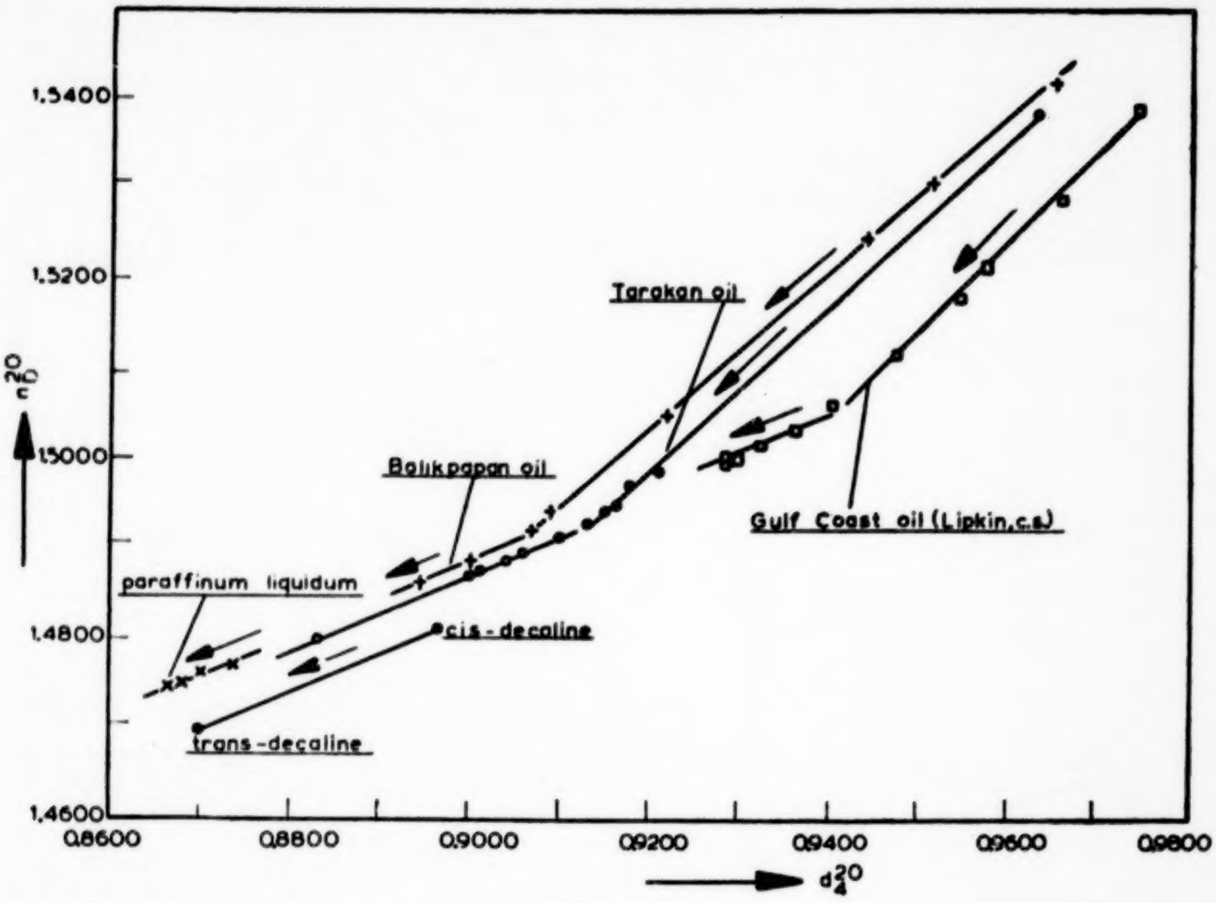


Fig. 1a.

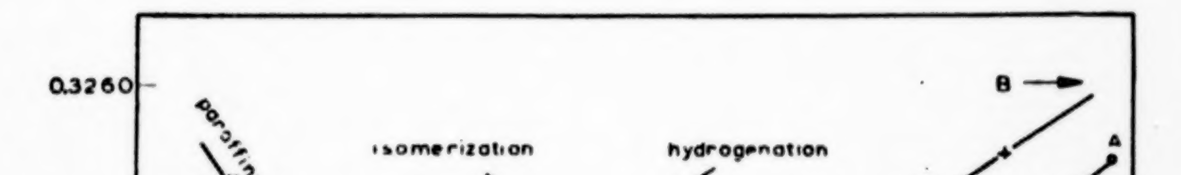


Fig. 1b.

Fig. 1. Treatment of aromatic mineral oil fractions with nickel on kieselguhr catalysts and high pressure hydrogen.

hydrogen may cause distinct changes in certain physical constants (refractive index, density, specific refraction, viscosity) of the saturated fractions, which changes show remarkable resemblance to those occurring in the *cis-trans* conversion of decalin under comparable conditions (*cf.* Fig. 1).

In all probability isomerizations of the same type take place during the prolonged hydrogenation. As follows from Fig. 1 these reactions bring about a small but obvious

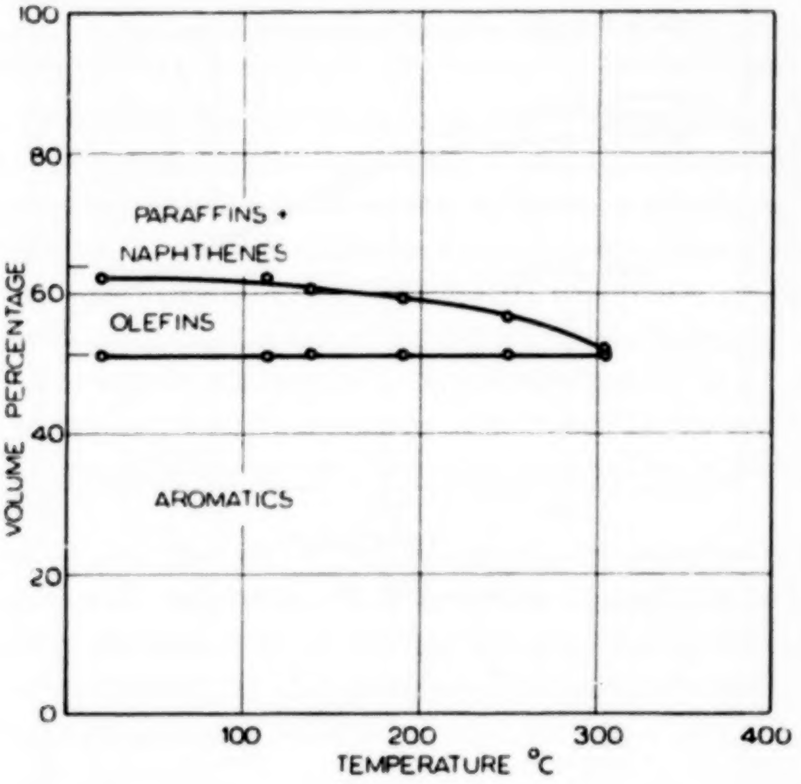


Fig. 2a.

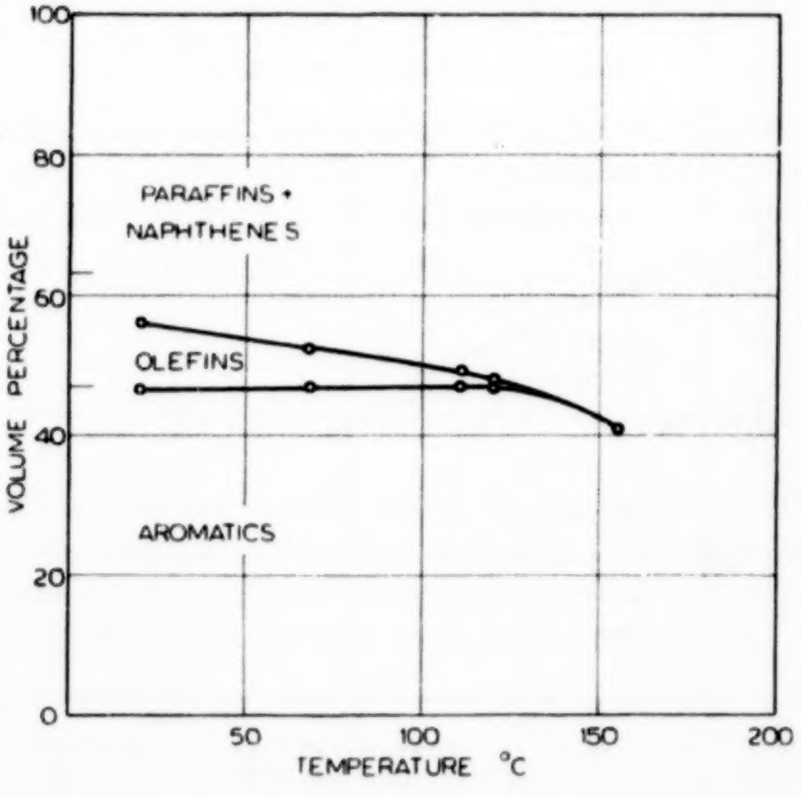


Fig. 2b.

Fig. 2a, b. Selective analytical hydrogenation of olefinic distillates.

References p. 507/509

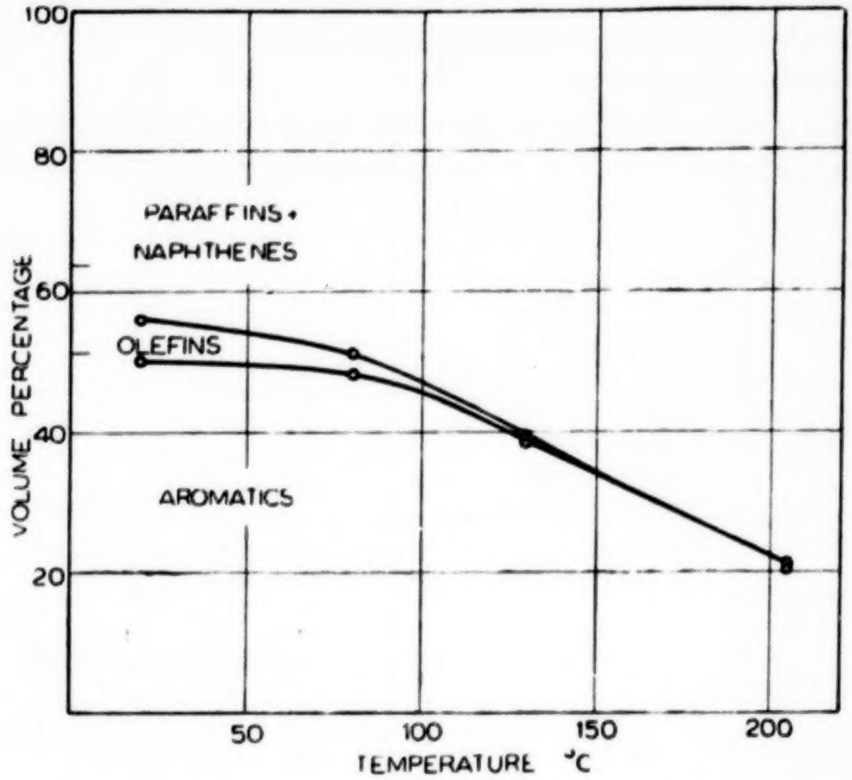


Fig. 2c.

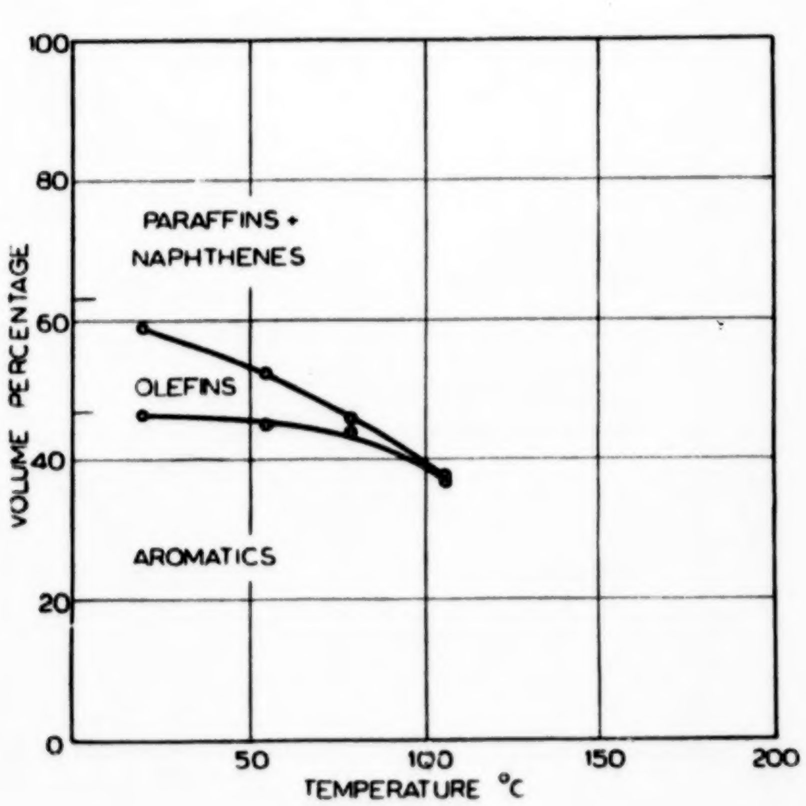


Fig. 2d.

Fig. 2c, d. Selective analytical hydrogenation of olefinic distillates.

increase of the specific refraction, and this is especially of importance with regard to the applicability of methods for ring analysis and carbon-type analysis based upon this function. Fortunately the isomerization process takes place very slowly. Only extremely prolonged reaction times (25-100 h) and relatively high temperatures (300-350°C) result in a pronounced isomerization of the oil, which might influence the results of graphical statistical analytical methods to some extent.

In normal cases the hydrogenation of mineral oil fractions can be used as an analytical tool for a quantitative transformation of aromatic rings into the corresponding naphthenes.

When *olefins* are present in the fractions to be investigated (this might be the case in, for instance, cracked products) it is sometimes useful to saturate the olefinic double bonds by a *selective* hydrogenation process, *viz.* without saturation of the aromatics. According to WATERMAN, WEBER AND ZWEEKHORST[4] especially molybdenum oxide on active carbon (100 atm hydrogen, 300°C, Fig. 2a) and platinum on silica-alumina (10 atm hydrogen, 120°C, Fig. 2b) are suitable for a selective hydrogenation of kerosine fractions, in contrast to other catalysts (*e.g.* Ni on kieselguhr, Fig. 2c, and Pd on active carbon, Fig. 2d) that are not strictly selective. This analytical hydrogenation of olefinic double bonds is especially useful for the evaluation of the constitution of cracked distillates.

When the problem of establishing the structure of hydrogenated products has been solved, more complicated mixtures, *e.g.* aromatic-containing fractions, can be considered. The existing methods of determining the composition of mineral oil fractions have been developed according to this scheme. The methods presented below are treated in principle in chronological order.

b. Ring analysis and carbon-type analysis of saturated mineral oil fractions

(*i*) *Original ring analysis of saturated mineral oil fractions*

The only unambiguous way of establishing the number of naphthenic rings R_N ($= R_T$) in saturated mineral oil fractions is by applying the Direct Method. This method involves the determination of the molecular weight M and the percentage hydrogen, %H. The number of rings in the saturated mixtures can then be calculated by means of the equation

$$R = 1 + (8.326 - 0.5793\%\text{H}) \cdot \frac{M}{100} \cdot \quad \ldots\ldots\ldots\ldots \quad (1)$$

A consequence of the presence of each ring in the average molecule of the fraction is that there are two hydrogen atoms lacking compared to the corresponding fraction with no ring, ***independent of the type of the ring*** (five-membered, six-membered ring, etc.) and of the way in which the various rings are linked.

If it is assumed that the number of carbon atoms in the average molecule of the oil fraction is c and the number of hydrogen atoms h then the molecular formula is C_cH_h. If the number of rings in the average molecule is R, this formula can also be represented by

$$C_cH_{2c-(2R-2)}.$$

For the molecular weight M it follows from the given molecular formula that

$$M = 12.010\,c + 1.008\,h \quad \ldots\ldots\ldots\ldots \quad (2)$$

and

$$M = 12.010\,c + 1.008\left\{2\,c - (2\,R - 2)\right\} \quad \ldots\ldots\ldots\ldots \quad (3)$$

The percentage of hydrogen %H is given by

$$\%\mathrm{H} = \frac{1.008\,h}{M}\,.\,100 \quad \ldots\ldots\ldots\ldots \quad (4)$$

or, on replacing h by $\dfrac{(M - 12.010\,c)}{1.008}$ according to equation (2):

$$\%\mathrm{H} = \frac{(M - 12.010\,c)}{M}\,.\,100 \quad \ldots\ldots\ldots\ldots \quad (5)$$

From equation (5) it follows for the value of c that

$$c = \frac{100M - \%\mathrm{H}\cdot M}{1201.0} \quad \ldots\ldots\ldots\ldots \quad (6)$$

Substitution of this value of c in equation (3) gives:

$$M = 12.010\,c + 2.016\,c - 2.016\,R + 2.016$$

$$R = \frac{-M}{2.016} + \frac{14.026(100M - \%\mathrm{H}\cdot M)}{1201.0 \times 2.016} + 1$$

or

$$R = 1 + (8.326 - 0.5793\,\%\mathrm{H})\,.\,\frac{M}{100} \quad \ldots\ldots\ldots\ldots \quad (1)$$

By means of equation (1) the number of rings in saturated mineral oil fractions can be calculated if %H and M are known.

The number of rings in saturated mixtures of hydrocarbons can also be read from the graph in Fig. 3, which represents equation (1) in the form

$$\%\mathrm{H} = 14.37 + \frac{172.6\,(1 - R)}{M} \quad \ldots\ldots\ldots\ldots \quad (7)$$

In this diagram lines of equal ring-number have been constructed, R increasing with 1 unit from top to bottom starting from a ring-number zero (paraffins). The diagram clearly shows the fact that with constant molecular weight the number of rings increases with a decreasing amount of hydrogen in the fractions considered. Special mention must be made of the fact that if $R = 1$, it follows that $\%\mathrm{H} = \dfrac{8.326}{0.5793} = 14.37$.

Though the method described is the only unambiguous one for ring determination in saturated hydrocarbon mixtures, it is rather laborious. Only experts can carry out the ultimate analysis to determine the hydrogen content with sufficient accuracy and it always takes much time. A method described by VLUGTER, WATERMAN AND VAN WESTEN[5] makes it possible to replace the hydrogen content by the specific refraction, defined according to LORENTZ-LORENZ[6], as

$$\frac{n^2 - 1}{n^2 + 2}\cdot\frac{1}{d}$$

where n = refractive index and d = density in g/ml.

Both the refractive index and the density are measured at the same temperature, *e.g.* 20°C. The refractive index is generally measured for the sodium D-line. In the fol-

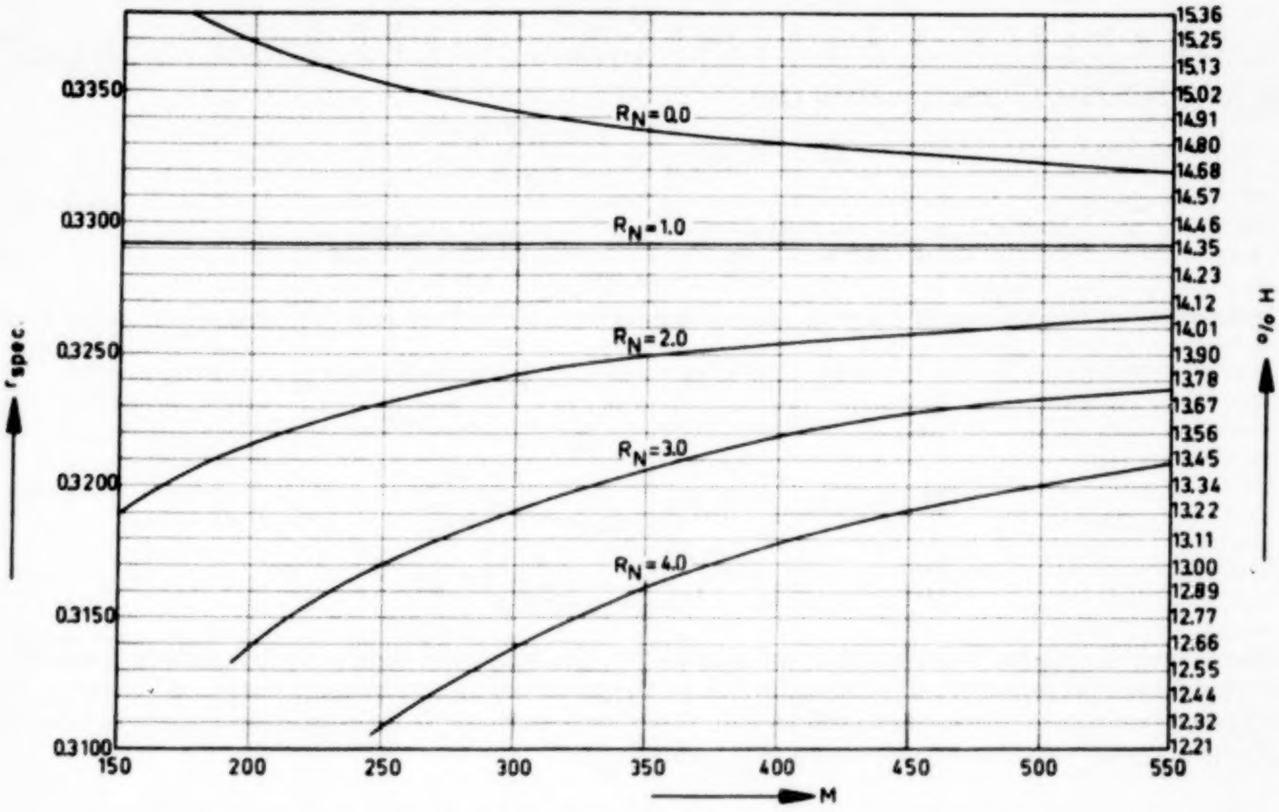


Fig. 3. Ring analysis diagram according to VLUGTER, WATERMAN AND VAN WESTEN.

lowing for reasons of conciseness, the specific refraction at 20°C will be indicated as $r^{20}_{\text{spec.}}$, omitting the symbol D sometimes used for indicating the sodium D-line*.

A diagram has been constructed from which it is possible to determine the number of rings of saturated mineral oil fractions if the specific refraction and the molecular weight are known (Fig. 3). The diagram is called the ring analysis diagram.

The possibility of using the specific refraction instead of the hydrogen content in the analysis of saturated mineral oil fractions is due to the fact that there exists a linear relationship between the specific refraction $r^{20}_{\text{spec.}}$ and the hydrogen content %H.

This can be elucidated by the following consideration.

If the molecular formula of the "average" molecule, which represents the mineral oil fraction under examination, is again taken as C_cH_h then

$$M = 12.010\,c + 1.008\,h \qquad \ldots\ldots\ldots\ldots\ldots \quad (2)$$

and

$$\%\text{H} = \frac{1.008\,h}{M} \,.\, 100 \qquad \ldots\ldots\ldots\ldots\ldots \quad (4)$$

The *specific refraction* is equal to the *molecular refraction* $\left(\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}\right)$ divided by the molecular weight M.

The *molecular refraction* $r_{\text{mol.}}$ is an additive function, *i.e.* it is a function which is equal to the sum of the atomic refraction of carbon, r_c, and that of hydrogen, r_h, each multiplied by its number of atoms in the "average" molecule:

$$\text{The molecular refraction } r_{\text{mol.}} = M.r^{20}_{\text{spec.}} = c.r_c + h.r_h \qquad \ldots\ldots \quad (8)$$

and

$$r^{20}_{\text{spec.}} = \frac{c.r_c + h.r_h}{M} \qquad \ldots\ldots\ldots\ldots\ldots \quad (9)$$

---

* The omission of D cannot give rise to confusion as in this monograph the wavelength of the sodium D-line is the principle wavelength at which refractions have been measured. If other wavelengths are used this is specially indicated.

From equation (4) it follows that

$$h = \frac{M.\%\mathrm{H}}{100.8} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (10)$$

and from equation (2) and equation (10)

$$M = 12.010\, c + \frac{1.008 M.\%\mathrm{H}}{100.8}$$

or

$$c = \left(M - \frac{M.\%\mathrm{H}}{100}\right).\frac{1}{12.010} = \frac{100 - \%\mathrm{H}}{1201.0}.M \quad \ldots\ldots\ldots\ldots \quad (11)$$

Substitution of the values of c and h, according to equations (10) and (11), in equation (9) gives:

$$r^{20}_{\mathrm{spec.}} = \frac{(100 - \%\mathrm{H}).\dfrac{M}{1201.0}.r_c + \dfrac{\%\mathrm{H}}{100.8}.M.r_h}{M}$$

$$r^{20}_{\mathrm{spec.}} = (100 - \%\mathrm{H}).\frac{r_c}{1201.0} + \frac{\%\mathrm{H}.r_h}{100.8}$$

$$r^{20}_{\mathrm{spec.}} = \frac{r_c}{12.010} + \left(\frac{r_h}{100.8} - \frac{r_c}{1201.0}\right)\%\mathrm{H} \quad \ldots\ldots\ldots\ldots \quad (12)$$

Since r_c and r_h can be considered as constants for the majority of the hydrocarbons present in saturated natural mineral oils (the influence of the presence of naphthenic rings, of branches, and of *cis-trans* isomers can be neglected in a first approximation), it follows from equation (12) that there is a linear relationship between $r^{20}_{\mathrm{spec.}}$ and %H.

The values of r_c and r_h have been calculated by EISENLOHR from "pure" substances[7]. This author gave the values $r_c = 2.418$ and $r_h = 1.100$. Substitution of these values in equation (12) gives:

$$r^{20}_{\mathrm{spec.}} = 0.20133 + 0.00890\ \%\mathrm{H} \quad \ldots\ldots\ldots\ldots \quad (13)$$

and

$$\%\mathrm{H} = 112.36\, r^{20}_{\mathrm{spec.}} - 22.620 \quad \ldots\ldots\ldots\ldots \quad (14)$$

If this value of %H is substituted in equation (1) the following relationship between $r^{20}_{\mathrm{spec.}}$, M and R_N is obtained:

$$R_N = 1 + \left\{8.326 - 0.5793\,(112.36\, r^{20}_{\mathrm{spec.}} - 22.620)\right\}\frac{M}{100}$$

or

$$R_N = 1 + (21.430 - 65.090\, r^{20}_{\mathrm{spec.}})\frac{M}{100} \quad \ldots\ldots\ldots\ldots \quad (15)$$

Thus it is possible to calculate the number of naphthenic rings of saturated oil fractions from the specific refraction and molecular weight by means of equation (15). The number of rings can also be determined from Fig. 4, in which the relationship between $r^{20}_{\mathrm{spec.}}$, M and R_N (besides that between %H, M and R_N) has been constructed by means of equation (15), which has been transformed into

$$r^{20}_{\mathrm{spec.}} = 0.3292 - \frac{(R_N - 1)\,1.536}{M} \quad \ldots\ldots\ldots\ldots \quad (16)$$

From equations (7) and (16) it follows that the curves representing fractions of equal ring-numbers in the %H - M and $r^{20}_{\mathrm{spec.}}$ - M diagram (Fig. 3) are hyperbolas. These curves become straight lines if %H - $\frac{1}{M}$ and $r^{20}_{\mathrm{spec.}}$ - $\frac{1}{M}$ plots are made instead. This is shown in Fig. 4.

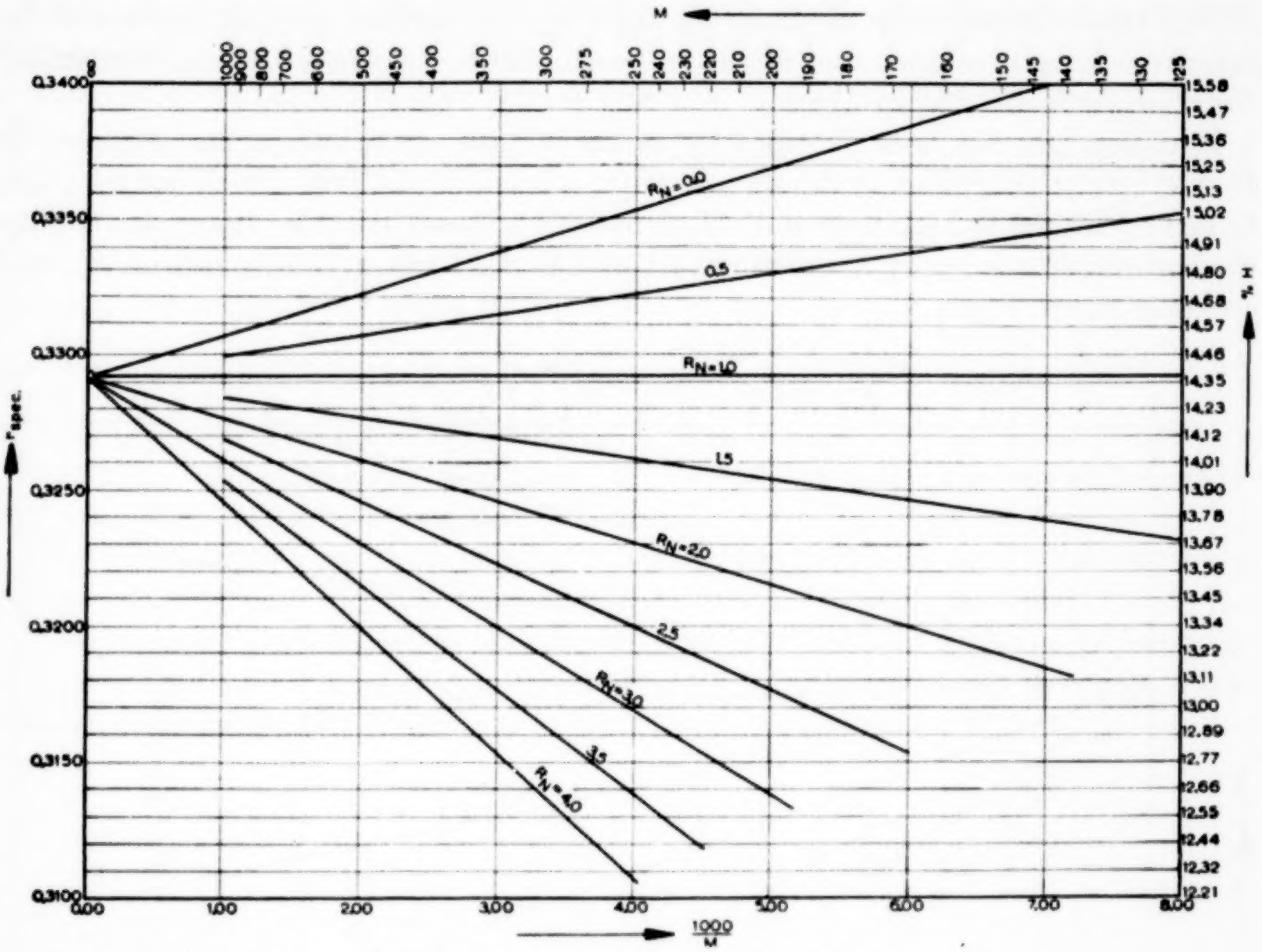


Fig. 4. $\%\text{H} - \frac{1}{M}$ and $r^{20}_{\text{spec.}} - \frac{1}{M}$ plots in connection with the ring-number of saturated mineral oil fractions.

The distances $\triangle r^{20}_{\text{spec.}}$ between the lines of equal ring-number for a definite value of the molecular weight are equal. This holds for both Fig. 3 and Fig. 4. This follows from equation (15)

$$R_N = 1 + (21.430 - 65.090\, r^{20}_{\text{spec.}})\, \frac{M}{100} \quad \ldots\ldots\ldots (15)$$

by writing

$$\triangle R_N = -65.090 \cdot \frac{M}{100} \cdot \triangle r^{20}_{\text{spec.}}$$

If $\triangle R_N = 1$ then

$$\triangle r^{20}_{\text{spec.}} = -\frac{1.5363}{M} \quad \ldots\ldots\ldots\ldots (17)$$

From this equation it follows that linear interpolation is permissible for the calculation of R_N from $r_{\text{spec.}}$ and M.

Recently another ring analysis diagram (Fig. 5) has been introduced by GEELEN, WATERMAN AND WESTERDIJK[8]. It has been constructed by means of the equation

$$r^{20}_{\text{spec.}} = 0.3310 + \frac{1.419 - 1.654\, R_N}{M} \quad \ldots\ldots\ldots\ldots (18)$$

taking $\frac{1}{M}$ as abcissa.

References p. 507/509

This equation has been obtained by applying the method of least squares to 81 saturated mineral oil fractions, of which the number of rings had been determined by the *n-d-M* method (*cf.* p. 418).

Equation (16) has been obtained by means of data of the substances available to EISENLOHR at that time. It differs somewhat from equation (18), which has been obtained by means of data from *n-d-M* analysis. The most notable difference is that the one-ring line in Fig. 5 does not run parallel to the horizontal axis, contrary to the one-ring line in Fig. 4.

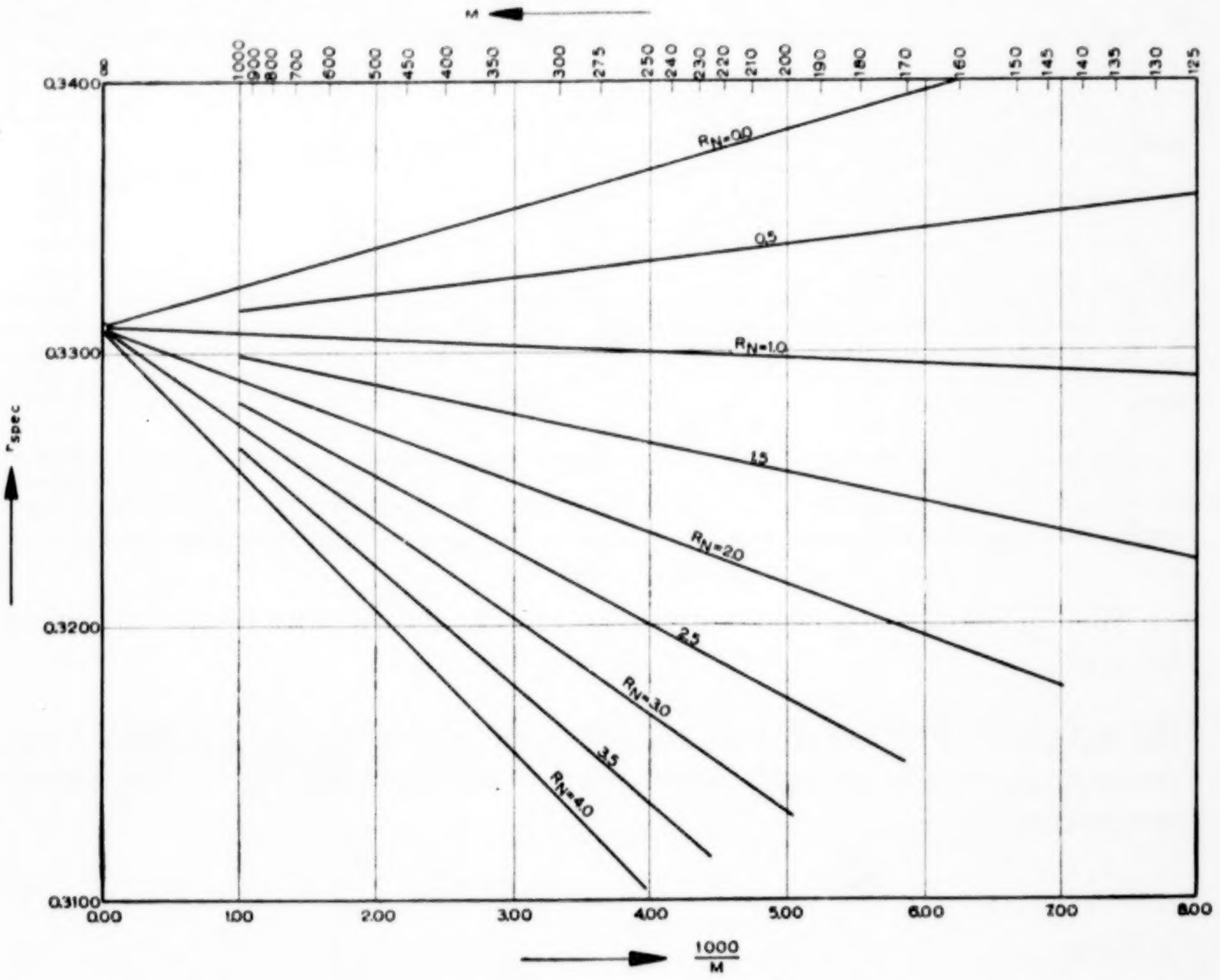


Fig. 5. Diagram representing the relationship between $r^{20}_{\text{spec.}}$, $\frac{1}{M}$ and R_N for saturated mineral oil fractions, based on *n-d-M* data.

The slope of the lines, *e.g.* in Fig. 5, can be determined by calculating the coefficient of $\frac{1}{M}$ in equation (18), the value being equal to $1.419 - 1.654\ R_N$. *E.g.* for $R_N = 1$ the slope is equal to -0.235.

It is also possible, as BOELHOUWER AND WATERMAN[9] have shown, to base a ring analysis diagram on physical constants of pure hydrocarbons belonging to homologous series (*n*-paraffins, *n*-alkyl-cyclopentanes, *n*-alkyl-cyclohexanes); in combination with the specific parachor this method permits a reliable determination of R_N in branched and non-branched saturated hydrocarbon mixtures of different origin: saturated mineral oil fractions, hydrogenated polymers, etc. (*cf.* Figs. 59 and 60 and p. 458).

Other methods have in the course of time been proposed for the determination of the number of rings in saturated mineral oil fractions.

BOOY AND WATERMAN[10] developed a diagram by plotting the specific refraction $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}$ against the dispersion $n_{G'} - n_C$ in connection with R_N of saturated mineral oil fractions (Fig. 6) ($n_{G'}$ and n_C are the refractive indices measured for the G′ and C lines of the hydrogen spectrum). A drawback of this method is that four physical constants have been used whilst in this case two are sufficient. In principle it must, however, be possible to replace n_D in the formula $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}$ by either n_C or $n_{G'}$, which reduces the number of physical constants to three.

STIJNTJES, WATERMAN AND WESTERDIJK[10a] introduced a diagram in which density was plotted against refractive index in connection with R_N (Fig. 7).

This was the first time that only *two* physical constants were used (the minimum number) to determine the ring-number of saturated mineral oil fractions.

A few other methods of determining the ring content of saturated mineral oil fractions will be discussed further on in connection with the application of the viscosity in the field of graphical statistical methods.

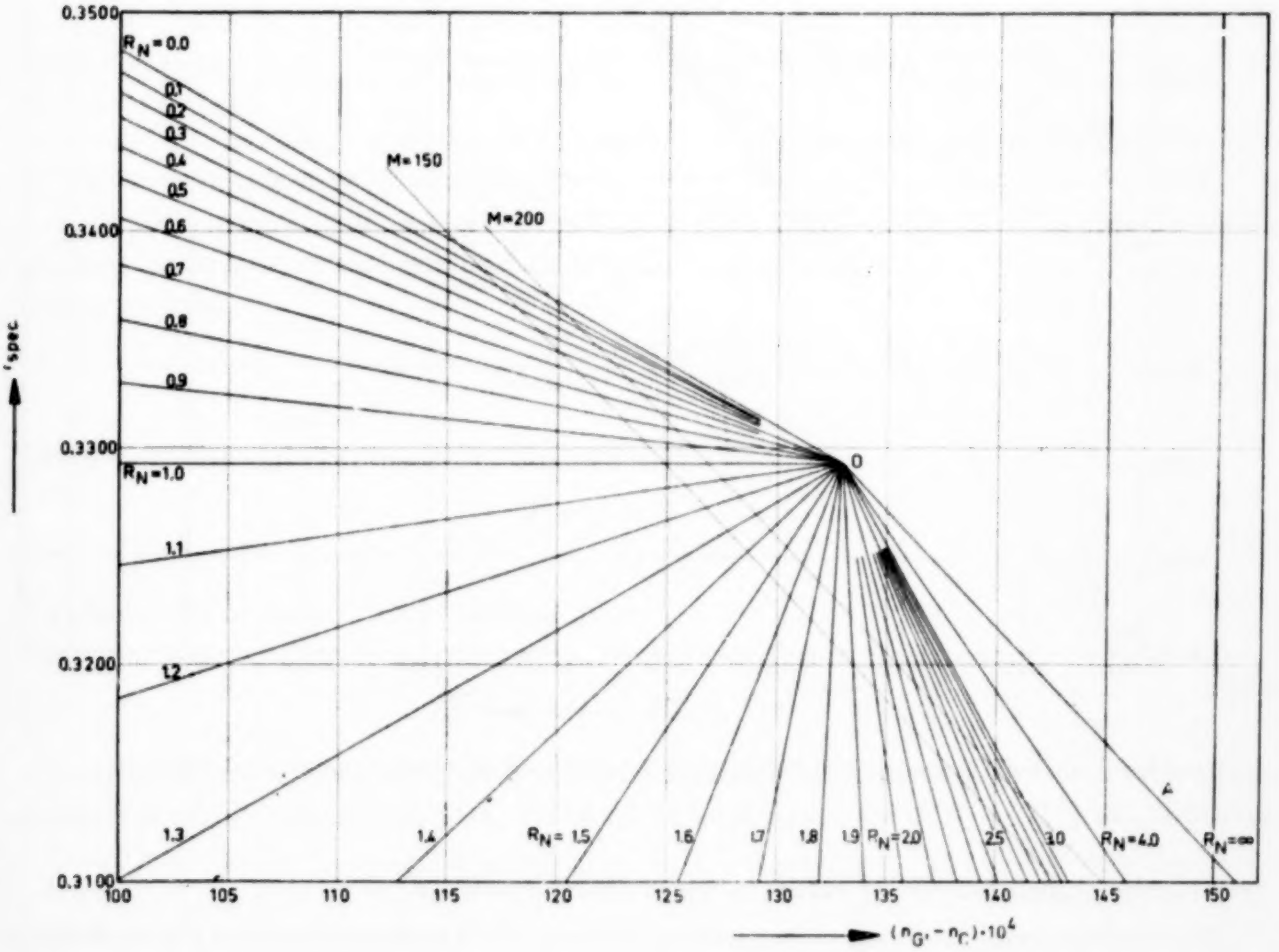


Fig. 6. $\left[\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}\right]$ – ($n_{G'}$ — n_C) diagram for the determination of R_N of saturated mineral oil fractions.

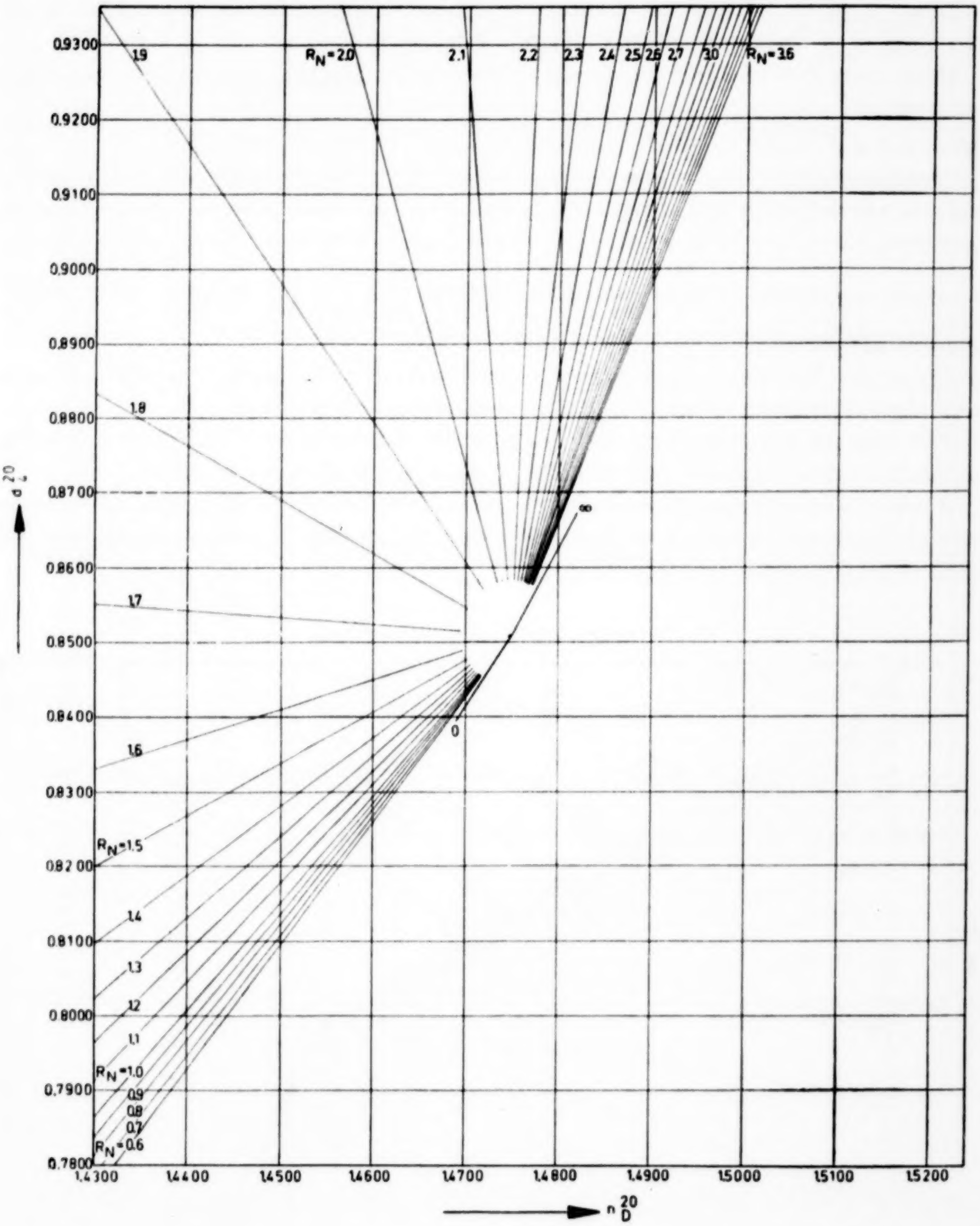


Fig. 7. *n–d* diagram for the determination of R_N of saturated mineral oil fractions.

(ii) Carbon-type analysis of saturated mineral oil fractions

The carbon-type analysis of saturated mineral oil fractions involves the determination of the percentage of carbon in naphthenic structure, $\%C_N$, which equals the percentage of carbon in ring structure, $\%C_R$. This can be done as follows.

If it is assumed that the ring-number of the saturated fraction is equal to R_N, the molecular weight equal to M and the molecular formula of the "average" molecule representing the oil fraction is $C_cH_{2c-(2R_N-2)}$ then

$$M = 12.010\,c + 1.008\,[2\,c - (2\,R_N - 2)] \quad \ldots\ldots\ldots \quad (3)$$

Now $\%C_R$ is defined as follows:

$$\%C_R = \frac{\text{number of C atoms in ring structure per molecule}}{\text{total number of carbon atoms per molecule}} \cdot 100$$

To determine the number of C atoms in ring structure from R_N, an assumption must be made concerning the type of the rings and the manner of fusion of the rings. Type and manner of fusion of the naphthenic rings may vary from one oil to another and because it is difficult as yet to obtain full information about this matter the determination of $\%C_N$ ($= \%C_R$) cannot be exact. However, in order to gain an approximate insight into the amount of carbon present in cyclic or non-cyclic structure the following assumptions are made.

(α) The rings only contain six carbon atoms.

(β) The molecules only contain kata-condensed molecules, *i.e.* molecules with the rings fused together in the same way as in naphthalene, anthracene, phenanthrene and the corresponding saturated compounds such as decalin. The consequences of deviations from these assumptions will be discussed later.

On the basis of these assumptions it can be said that the first ring present in the molecule contains six carbon atoms and each following ring adds four carbon atoms to this number.

Therefore two cases must be distinguished: 1. The ring-number of the fraction $\leqslant 1$, 2. The ring-number of the fraction $\geqslant 1$.

1. If the ring-number of the fraction $\leqslant 1$ then the total number of carbon atoms present in ring structure is equal to $6\,R_N$.
Consequently

$$\%C_R = \frac{6\,R_N}{c} \cdot 100$$

From equation (3) it follows for the value of c that

$$c = \frac{M + 1.008\,(2\,R_N - 2)}{14.026} \quad \ldots\ldots\ldots \quad (3a)$$

Combination of these two equations gives

$$\%C_R = \frac{3\,R_N \cdot 2805.2}{M + 2.016\,(R_N - 1)} \quad \ldots\ldots\ldots \quad (19)$$

2. If the ring-number of the fraction under examination $\geqslant 1$ then the total number of carbon atoms present in ring structure is equal to $6 + (R_N - 1)\,4$. In this case

$$\%C_R = \frac{6 + 4\,R_N - 4}{c} \cdot 100 = \frac{2(2\,R_N + 1)}{c} \cdot 100$$

Insertion of the value of c from equation (3a) gives

$$\%C_R = \frac{(2\,R_N + 1)\,2805.2}{M + 2.016(R_N - 1)} \quad \ldots\ldots\ldots \quad (20)$$

On combining equation (15) with equation (19) and (20), respectively, $r^{20}_{\text{spec.}}$ can be expressed as follows:

$$1.\ \text{if } R_N \leqslant 1 : r^{20}_{\text{spec.}} = \frac{\dfrac{8415.6}{M} + 1803.5 - 1.432\ \%C_R}{5477.7 - 1.3122\ \%C_R} \quad \ldots\ldots (21)$$

$$2.\ \text{if } R_N \geqslant 1 : r^{20}_{\text{spec.}} = \frac{\dfrac{8415.6}{M} + 1202.3 - 1.432\ \%C_R}{3651.8 - 1.3122\ \%C_R} \quad \ldots\ldots (22)$$

For a particular value of $\%C_R$ there exists a linear relationship between $r^{20}_{\text{spec.}}$ and $\frac{1}{M}$, which follows from equations (21) and (22). This makes it possible to construct the lines of equal values of $\%C_R$ in a $r^{20}_{\text{spec.}}$ - $\frac{1}{M}$ diagram in a simple manner (Fig. 8).

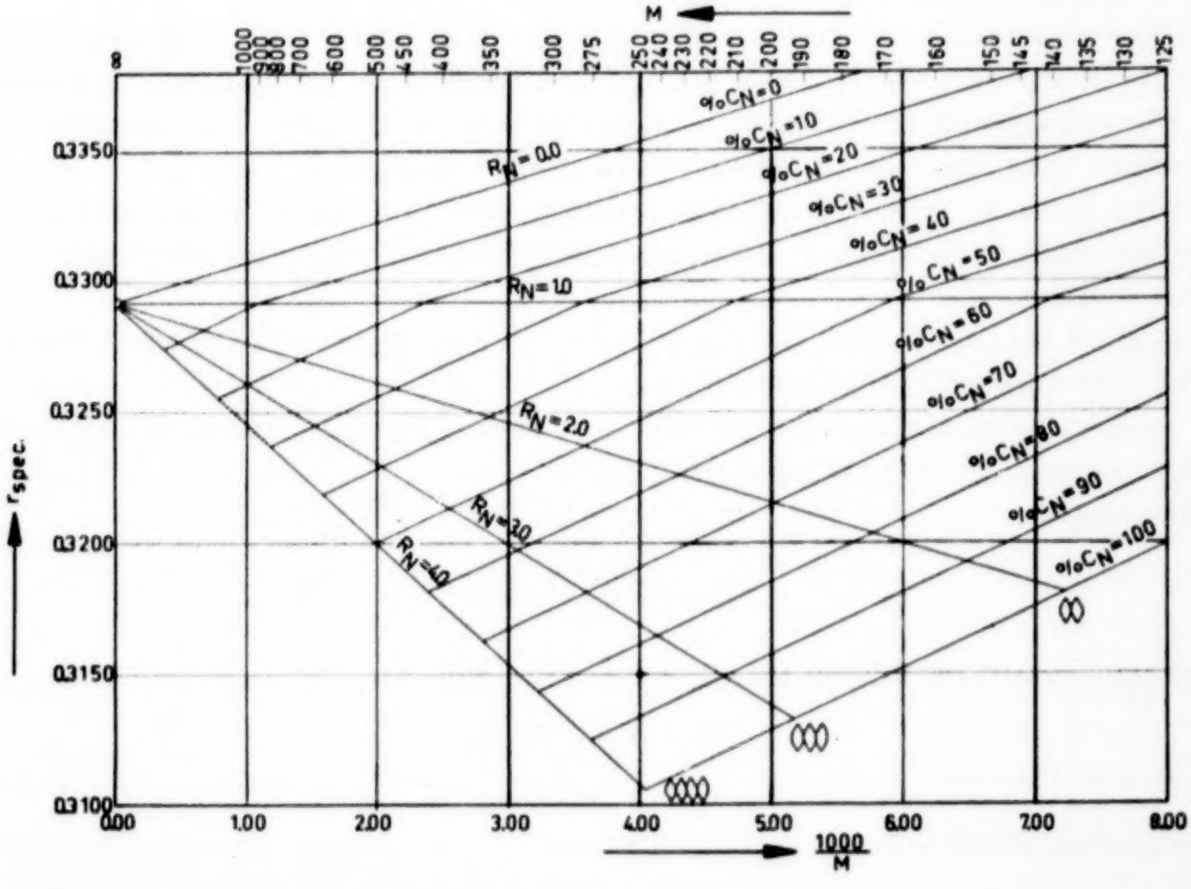


Fig. 8. Diagram representing the $r^{20}_{\text{spec.}}$ - $\frac{1}{M}$ relationship of saturated mineral oil fractions in connection with R_N and $\%C_R$ (= $\%C_N$).

The fact that two regions have to be used to calculate the value of $\%C_R$, *viz.* one in which $R_N \leqslant 1$ and one in which $R_N \geqslant 1$, gives rise to another reason why $\%C_R$ is no exact measure for the percentage of carbon atoms present in ring structure. This is also illustrated by the fact that in Fig. 8 the lines for equal $\%C_R$ show a discontinuity at $R_N = 1$.

To show the influence of possible wrong assumptions on the value of $\%C_R$ the following example may be given.

Example: The average molecule of a saturated mineral oil fraction contains 0.9 rings. This fraction is composed of molecules containing 20 carbon atoms. The following 6 cases I, II, III, IV, V and VI will be considered. In cases I, II, III and IV it is supposed that 70% of the molecules in the oil contain one ring per molecule, 20% of the molecules contain no rings and 10% of the molecules contain two rings per molecule, whilst molecules with three rings or more do not occur in appreciable amount. This supposition seems to be in agreement with the real situation in many mineral oil fractions. In cases V and VI it is supposed that 90% of the molecules of the fraction contain one ring per molecule and 10% of the molecules contain no ring.

I. In the molecules with two rings the rings are kata-condensed and the different rings contain *six* carbon atoms per ring. In this case

$$\%C_R = 70 \cdot \frac{6}{20} + 20 \cdot \frac{0}{20} + 10 \cdot \frac{10}{20} = 21 + 0 + 5 = 26\%.$$

II. In the molecules with two rings the rings are kata-condensed and the different rings contain *five* carbon atoms per ring. Then

$$\%C_R = 70 \cdot \frac{5}{20} + 20 \cdot \frac{0}{20} + 10 \cdot \frac{8}{20} = 17.5 + 0 + 4 = 21.5\%.$$

III. The molecules with two rings contain two separate rings and the different rings contain *six* carbon atoms per ring. In this case

$$\%C_R = 70 \cdot \frac{6}{20} + 20 \cdot \frac{0}{20} + 10 \cdot \frac{12}{20} = 21 + 0 + 6 = 27\%.$$

IV. The molecules with two rings contain two separate rings and the various rings contain *five* carbon atoms per ring. Then

$$\%C_R = 70 \cdot \frac{5}{20} + 20 \cdot \frac{0}{20} + 10 \cdot \frac{10}{20} = 17.5 + 0 + 5 = 22.5\%.$$

V. Molecules with two rings do not occur and the rings contain *six* carbon atoms per ring. The $\%C_R$ amounts to

$$\%C_R = 90 \cdot \frac{6}{20} + 10 \cdot \frac{0}{20} = 27 + 0 = 27\%.$$

VI. Molecules with two rings do not occur and the rings contain *five* carbon atoms per ring. Then

$$\%C_R = 90 \cdot \frac{5}{20} + 10 \cdot \frac{0}{20} = 22.5 + 0 = 22.5\%.$$

From these examples it can be concluded that if $R_N \leqslant 1$ the greatest influence on $\%C_R$ is exerted by the replacement of six-membered rings by five-membered rings (*cf.* I and II, III and IV, V and VI).

The influence of the replacement of kata-condensed by non-condensed rings (*cf.* I and III, III and V) and the two-ring systems by one-ring systems (*cf.* I and III with V, II and IV with VI) (if $R \leqslant 1$) is much smaller.

If $R \geqslant 1$ then the influence of the way in which the molecules are linked (kata-condensed or non-kata-condensed) becomes greater as the ring-number increases.

Besides constructing lines for equal ring-number or equal $\%C_R$ values in the ring analysis diagram, it is also possible to construct lines of equal values of the aniline point[3] and the density[3]. This is shown in Figs. 9 and 10 respectively.

Thus it is possible to determine the value of the aniline point (A.P.) of a saturated mineral oil fraction by means of Fig. 9 if the specific refraction and the molecular weight are known.

From Fig. 10 it is possible to determine the value of the specific refraction if M and d are known. From the value of the specific refraction thus determined and the experimental value of the density the refractive index can be determined.

An example has been given here of the correlation existing between physical constants of saturated mineral oil fractions. Other examples will be given when the viscosity is discussed.

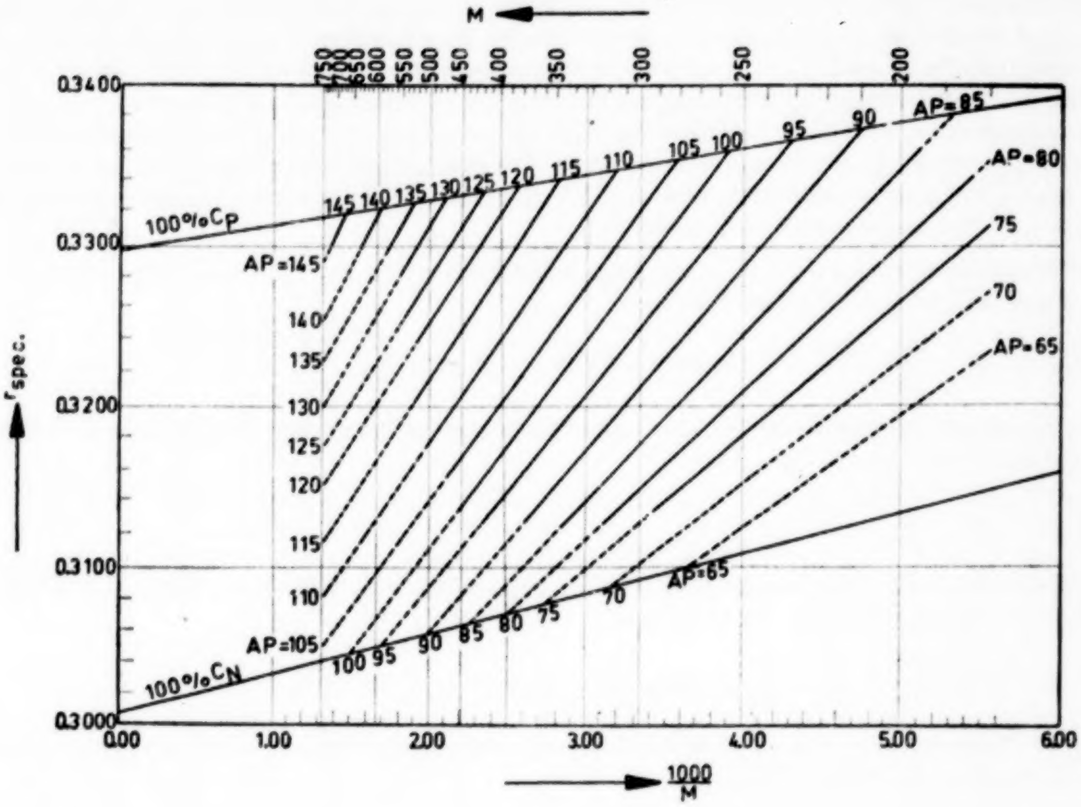


Fig. 9. Diagram representing the $r^{20}_{\text{spec.}} - \frac{1}{M}$ relationship in connection with R_N and the aniline point. (Saturated mineral oil fractions).

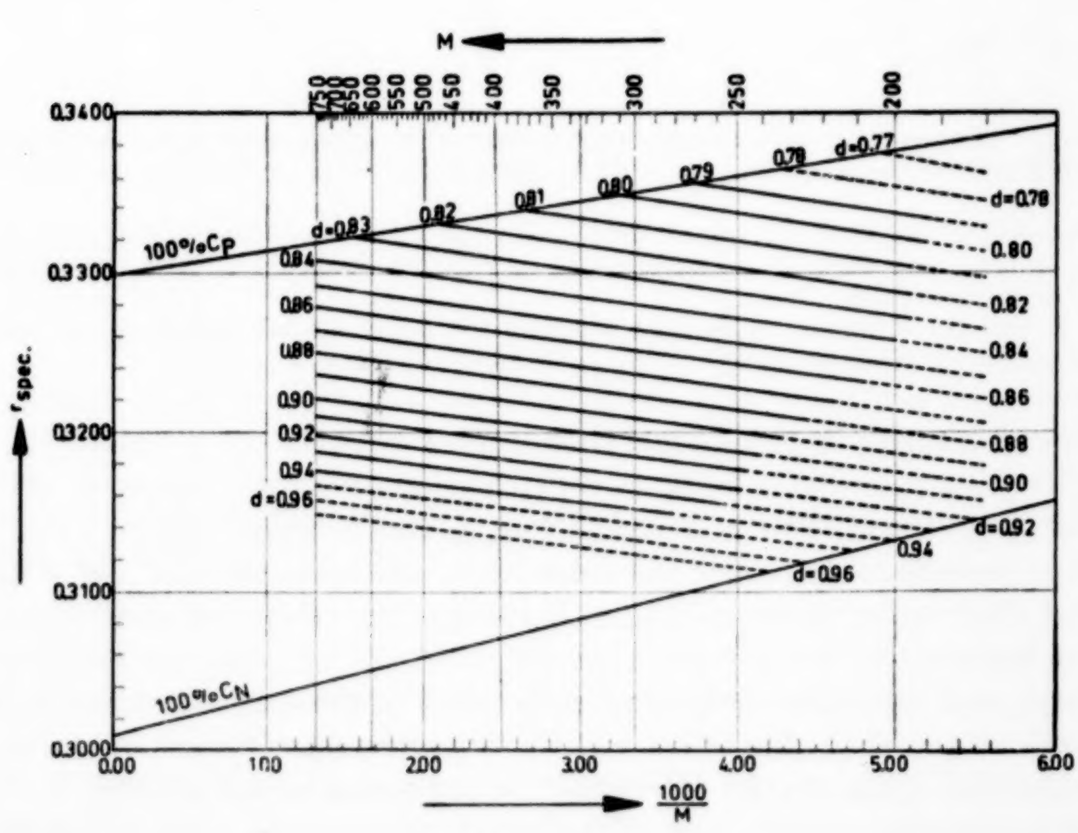


Fig. 10. Diagram representing the $r^{20}_{\text{spec.}} - \frac{1}{M}$ relationship in connection with R_N and density. (Saturated mineral oil fractions).

c. Ring analysis and carbon-type analysis of natural mineral oil fractions by means of the Direct Method

(i) Determination of $\%C_A$

If no cracking, ring opening or ring closure takes place during the hydrogenation and no "foreign" elements (elements other than carbon and hydrogen) are present in the mineral oil fraction, the equation for determining the $\%C_A$ can be derived as follows.

Defining the hydrogen content before and after complete hydrogenation as $\%H_o$ and $\%H$, respectively, the molecular weight before and after hydrogenation as M_o and M, respectively, and the molecular formulae before and after hydrogenation as $C_cH_{h_o}$ and C_cH_h, respectively (the number of carbon atoms remaining constant during the hydrogenation), the following relation holds:

$$\%C_A = \frac{\text{number of carbon atoms per molecule in aromatic structure}}{\text{total number of carbon atoms present in the average molecule}} \cdot 100$$

or

$$\%C_A = \frac{h - h_o}{c} \cdot 100 \quad \text{. . . . .} \quad (23)$$

From equation (4) it follows that

$$h = \frac{\%H \cdot M}{1.008 \cdot 100} \text{ and } h_o = \frac{\%H \cdot M_o}{1.008 \cdot 100}$$

and from equation (6)

$$c = \frac{100\,M - \%H \cdot M}{1201.0} \quad \text{. . . . .} \quad (6)$$

Substitution of h, h_o and c in equation (23) gives

$$\%C_A = \frac{\dfrac{\%H \cdot M}{1.008} - \dfrac{\%H_o \cdot M_o}{1.008}}{100\,M - \%H \cdot M} \cdot 1201.0$$

or

$$\%C_A = 1191 \cdot \frac{\%H - \%H_o \cdot \dfrac{M_o}{M}}{100 - \%H} \quad \text{. . . . .} \quad (24)$$

By means of equation (24) it is possible to calculate the value of $\%C_A$ of mineral oil fractions if molecular weight and hydrogen content of both the original and the saturated fraction are known. Olefinic compounds should be absent.

The value of $\%C_A$ calculated in this way is exact; however, the method requires much practical experience (*cf.* p. 404). Since M and M_o are almost equal, certainly within the experimental error, $\%C_A$ is practically independent of the molecular weight.

(ii) Determination of the total ring-number R_T

After complete hydrogenation of the mineral oil fraction the total ring content can be determined in the same way as has been described for the saturated fractions, *viz.* by applying equation (1) (p. 403):

$$R_T = 1 + (8.326 - 0.5793\,\%H) \cdot \frac{M}{100} \quad \text{. . . . .} \quad (1a)$$

where %H = hydrogen content of the saturated oil fraction
and M = molecular weight of the saturated oil fraction.

No assumptions regarding the ring type or the extent to which the rings are condensed need be made; R_T is an exact value, inasmuch as M can be considered to be determinable in practice.

(*iii*) *Determination of* $\%C_R$

After the complete hydrogenation of the mineral oil fractions use can once again be made of the equations that have been derived for saturated mineral oil fractions on the assumption that six-membered rings are present and that the rings in the multiple ring systems are kata-condensed. The equations are :

if $R_T \leqslant 1$

$$\%C_R = \frac{3\,R_T \cdot 2805.2}{M + 2.016(R_T - 1)} \quad \ldots\ldots\ldots\ldots \quad (19a)$$

if $R_T \geqslant 1$

$$\%C_R = \frac{(2\,R_T + 1)2805.2}{M + 2.016\,(R_T - 1)} \quad \ldots\ldots\ldots\ldots \quad (20a)$$

(*iv*) *Determination of the number of aromatic rings* R_A

The number of aromatic rings R_A in mineral oil fractions can be calculated from $\%C_A$ (eqn. 24):

$$\%C_A = 1191 \cdot \frac{\%H - \%\,H_\circ \cdot \dfrac{M_\circ}{M}}{100 - \%H} \quad \ldots\ldots\ldots\ldots \quad (24)$$

and the molecular weight. The value of R_A cannot be determined with exactitude. Nevertheless, a reasonable approximation may be obtained by assuming that multiple aromatic ring systems are kata-condensed. It is almost certain that only six-membered aromatic rings occur.

Two cases must be distinguished: (α) the ring-number of the fraction $\leqslant 1$, (β) the ring-number of the fraction $\geqslant 1$.

(α) If the ring-number of the fraction $\leqslant 1$ and there are no molecules present that contain more than one ring, then the total number of carbon atoms present in aromatic structure is equal to $6\,R_A$. According to the definition of $\%C_A$ the following equation holds true:

$$\%C_A = \frac{6\,R_A}{c} \cdot 100 \quad \ldots\ldots\ldots\ldots \quad (25)$$

The number of hydrogen atoms in the average molecule amounts to

$$h_\circ = 2\,c - (8\,R_A - 2) \quad \ldots\ldots\ldots\ldots \quad (26)$$

if $R_A \leqslant 1$.

One aromatic ring causes a deficiency of 8 hydrogen atoms compared to an alkane with the same number of carbon atoms. This explains the term $8\,R_A$ in equation (26).

From equation (26) it follows for the molecular weight that

$$M = 12.010\,c + 1.008\,\{2\,c - (8\,R_A - 2)\} \quad \ldots\ldots \quad (27)$$

Equation (27) gives for the value of c

$$c = \frac{M + 1.008\,(8\,R_A - 2)}{14.026} \qquad \ldots\ldots\ldots\ldots (28)$$

Introducing this value of c into equation (25) gives:

$$\%C_A = \frac{6\,R_A \cdot 14.026}{M + 1.008(8\,R_A - 2)} \cdot 100 \qquad \ldots\ldots\ldots\ldots (29)$$

$$\%C_A \cdot M + 8.064\,R_A \cdot \%C_A - 2.016\,\%C_A = 84.156\,R_A \cdot 100$$

or

$$R_A = \frac{(M - 2.016)\,\%C_A}{8415.6 - 8.064\,\%C_A} \qquad \ldots\ldots\ldots\ldots (30)$$

(β) If the number of aromatic rings present in mineral oil fractions $\geqslant 1$, the number of aromatic carbon atoms present in the average molecule is equal to

$$6 + (R_A - 1)\,4 = 2 + 4\,R_A.$$

From the definition of $\%C_A$ the following equation is obtained:

$$\%C_A = \frac{2 + 4\,R_A}{c} \cdot 100 \qquad \ldots\ldots\ldots\ldots (31)$$

The number of hydrogen atoms present in the average molecule can be put equal to

$$h_o = 2\,c - 6\,R_A \qquad \ldots\ldots\ldots\ldots (32)$$

This can be explained as follows.

The number of hydrogen atoms present in an alkane with the same number of carbon atoms is $2\,c + 2$. The presence of the first aromatic ring results in a decrease of eight hydrogen atoms, each further aromatic ring causes a decrease of a further six hydrogen atoms if the rings are kata-condensed (two for the ring closure, four for the replacement of CH_2 groups by CH groups). The overall result is the presence of $(2\,c + 2) - 8 - (R_A - 1)\,6 = 2\,c - 6\,R_A$ hydrogen atoms in the average molecule representing the mineral oil fraction.

The molecular weight of the fraction is

$$M = 12.010\,c + 1.008\,(2\,c - 6\,R_A) \qquad \ldots\ldots\ldots\ldots (33)$$

From this equation it follows for the value of c

$$c = \frac{M + 1.008 \cdot 6\,R_A}{14.026} \qquad \ldots\ldots\ldots\ldots (34)$$

Introducing this value of c into equation (31) gives:

$$\%C_A = \frac{(2 + 4\,R_A)\,14.026}{M + 1.008 \cdot 6\,R_A} \cdot 100 \qquad \ldots\ldots\ldots\ldots (35)$$

$$\%C_A \cdot M + 6\,R_A \cdot 1.008 \cdot \%C_A = 5610.4\,R_A + 2805.2$$

$$R_A = \frac{\%C_A \cdot M - 2805.2}{5610.4 - 6.048\,\%C_A} \qquad \ldots\ldots\ldots\ldots (36)$$

By means of equations (30) and (36) it is possible to calculate the number of aromatic rings per average molecule of mineral oil fractions with $R_A \leqslant 1$ and $R_A \geqslant 1$, respectively, from the molecular weights and the percentages of carbon atoms in aromatic structure. The calculated values are not exact values since it is assumed that the multiple ring systems are kata-condensed; however, this often seems to be the case.

(*v*) *Determination of the number of naphthenic rings* R_N

As the values of R_T and R_A can be determined in the way described above, it is possible to determine the value of R_N of mineral oil fractions

$$R_N = R_T - R_A \qquad (37)$$

The curious fact has been discovered by GEELEN, WATERMAN AND WESTERDIJK[11] that this value can also be obtained by applying the ring analysis diagram (derived for saturated mineral oil fractions for the determination of R_N, previously described) to a mineral oil fraction, by using its specific refraction and molecular weight. The value of R_N read from the diagram (Fig. 3) appears to be equal to the number of naphthenic rings present in the mineral oil fraction that contains aromatic compounds. It means that balancing influences are operating, which cause the aromatic part of the average molecule to behave as the paraffinic part. This property is a remarkable feature of natural mineral oil fractions (*cf.* also 5*b (i)*, p. 465).

(*vi*) *Determination of* $\%C_N$

Once the percentage of carbon in aromatic structure, $\%C_A$, and the percentage of carbon in ring structure, $\%C_R$, are known, the percentage of carbon in naphthenic structure, $\%C_N$, follows from the equation:

$$\%C_N = \%C_R - \%C_A \qquad (38)$$

If the diagram derived for saturated fractions is used where $r^{20}_{\text{spec.}}$ is plotted against $\frac{1}{M}$ in connection with R_N and $\%C_R$ (Fig. 8), a value of $\%C_R$ is read by using the values of $r^{20}_{\text{spec.}}$ and $\frac{1}{M}$ for the mineral oil fraction. For the same reasons as described under *(v)* this value of $\%C_R$ proves to be equal to the value obtained according to equation (38).

d. Ring analysis and carbon-type analysis of mineral oil fractions by means of the n-d-M method

In the *n-d-M* method use is made of *three physical constants*, namely the refractive index *n* (measured for the sodium D-line), the density *d* in g/ml and the molecular weight *M*, for the determination of the composition of mineral oil fractions.

This is not the first time that *physical constants only* were used to determine the structural composition of non-hydrogenated mineral oil fractions. VLUGTER, WATERMAN AND VAN WESTEN[5] had already proposed using the specific refraction, aniline point and molecular weight of the fraction. The predicted value of the aniline point, obtained by means of the diagram presented in Fig. 9, was compared with the experimental value. The difference △AP was a measure for the percentage of carbon in aromatic structure, $\%C_A$. Instead of the aniline point, the density can be used in an analogous way. The difference △*d*[3,12] then replaces △AP as a measure for $\%C_A$.

The *n-d-M* method, which has been generally adopted nowadays for the ring analysis and the carbon-type analysis of mineral oils, both hydrogenated and non-hydrogenated, is a further development of these investigations. The method has been described in detail by LEENDERTSE, TADEMA, SMITTENBERG, VLUGTER, WATERMAN, VAN WESTEN AND VAN NES[3,12]. It is based on the fact that there is a linear relationship between the percentage of carbon, %C (in either naphthenic, aromatic or paraffinic structure) and the refractive index, the density and the reciprocal molecular weight, according to the equation:

$$\%C = \frac{a}{M} + b\triangle d + c\triangle n \quad \ldots\ldots\ldots\ldots \quad (39)$$

where a, b and c are constants,

$$\triangle d = d - d_\infty$$
$$\triangle n = n - n_\infty$$

d_∞ and n_∞ are the values of the refractive index and density, respectively, of the hypothetical normal hydrocarbon with infinite chain length. For the number of rings (either naphthenic or aromatic rings or total number of rings) an analogous equation is valid:

$$R = a' + b'M\triangle d + c'M\triangle n \quad \ldots\ldots\ldots \quad (39a)$$

a', b' and c' are constants different from a, b and c. The determination of the constants mentioned in equations (39) and (39a) have been described by VAN NES AND VAN WESTEN[3,12] and will not be repeated here. The results are reported in Table I.

TABLE I

FORMULAE OF THE n-d-M METHOD

	Measurements at 20°C		*Measurements at 70°C*
	$v = 2.51\,(n - 1.4750) - (d - 0.8510)$ $w = (d - 0.8510) - 1.11(n - 1.4750)$		$x = 2.42\,(n - 1.4600) - (d - 0.8280)$ $y = (d - 0.8280) - 1.11(n - 1.4600)$
$\%C_A$	If v is positive $\%C_A = 430\,v + \frac{3660}{M}$ If v is negative $\%C_A = 670\,v + \frac{3660}{M}$	$\%C_A$	If x is positive $\%C_A = 410\,x + \frac{3660}{M}$ If x is negative $\%C_A = 720\,x + \frac{3660}{M}$
$\%C_R$	If w is positive $\%C_R = 820\,w - 3S + \frac{10000}{M}$ If w is negative $\%C_R = 1440\,w - 3S + \frac{10600}{M}$	$\%C_R$	If y is positive $\%C_R = 775\,y - 3S + \frac{11500}{M}$ If y is negative $\%C_R = 1400\,y - 3S + \frac{12100}{M}$
$\%C_N$ $\%C_P$	$\%C_N = \%C_R - \%C_A$ $\%C_P = 100 - \%C_R$	$\%C_N$ $\%C_P$	$\%C_N = \%C_R - \%C_A$ $\%C_P = 100 - \%C_R$
R_A	If v is positive $R_A = 0.44 + 0.055\,Mv$ If v is negative $R_A = 0.44 + 0.080\,Mv$	R_A	If x is positive $R_A = 0.41 + 0.055\,Mx$ If x is negative $R_A = 0.41 + 0.080\,Mx$
R_T	If w is positive $R_T = 1.33 + 0.146M(w - 0.005S)$ If w is negative $R_T = 1.33 + 0.180M(w - 0.005S)$	R_T	If y is positive $R_T = 1.55 + 0.146M(y - 0.005S)$ If y is negative $R_T = 1.55 + 0.180M(y - 0.005S)$
R_N	$R_N = R_T - R_A$	R_N	$R_N = R_T - R_A$

S is weight percentage of sulphur.

By means of the equations given in Table I the various values of $\%R$ can be calculated if n, d and M are known.

If sulphur is present a correction must be made in the case of $\%C_R$ and R_T. This correction is given in the equation for $\%C_R$ and R_T, where the weight% of sulphur is denoted as S. No correction has to be applied to $\%C_A$ and R_A for the presence of sulphur.

Should data at some other temperature, say 40°C, be available, then similar equations as listed in Table I are valid. The numerical values of the constants of these equations can be obtained by linear interpolation of the values of the constants given in the table for 20°C and 70°C.

The n-d-M method for determining the composition of olefin-free mineral oil fractions has proved to be reliable if $\%C_R \leqslant 75$ with the further limitation that $\%C_A \leqslant 1\frac{1}{2}\ \%C_N$. For the number of rings the limitation is $R_T \leqslant 4$ with $R_A \leqslant \frac{1}{2}\ R_T$.

The method is also applicable to olefin-free paraffin waxes, residual oils and oils containing less than 2% sulphur, 0.5% oxygen and 0.5% nitrogen.

The method has the fundamental drawback that different numerical constants have to be used in the formulae, depending on the range considered. However, the practical application is not hampered by this fact.

e. Kinematic viscosity and structure of mineral oil fractions

(*i*) *Structure of saturated mineral oil fractions: ν-M diagrams and ν-n diagram*

In the last few years the kinematic viscosity and its temperature dependence have been used for the determination of the composition of mineral oil fractions. The first steps in this field were made by BOELHOUWER, VAN STEENIS AND WATERMAN[13], who

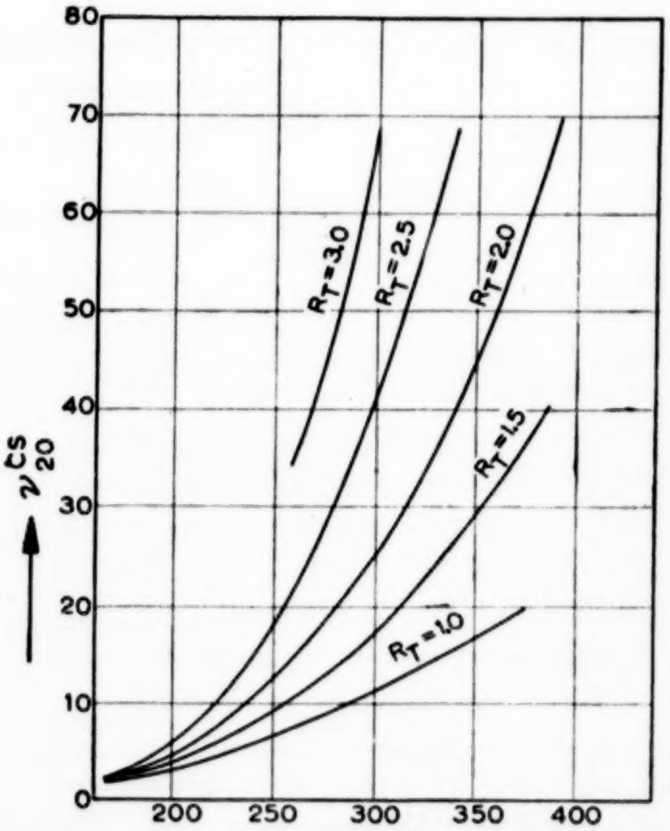


Fig. 11. ν-M diagram for determining the number of rings per molecule in saturated mineral oil fractions.

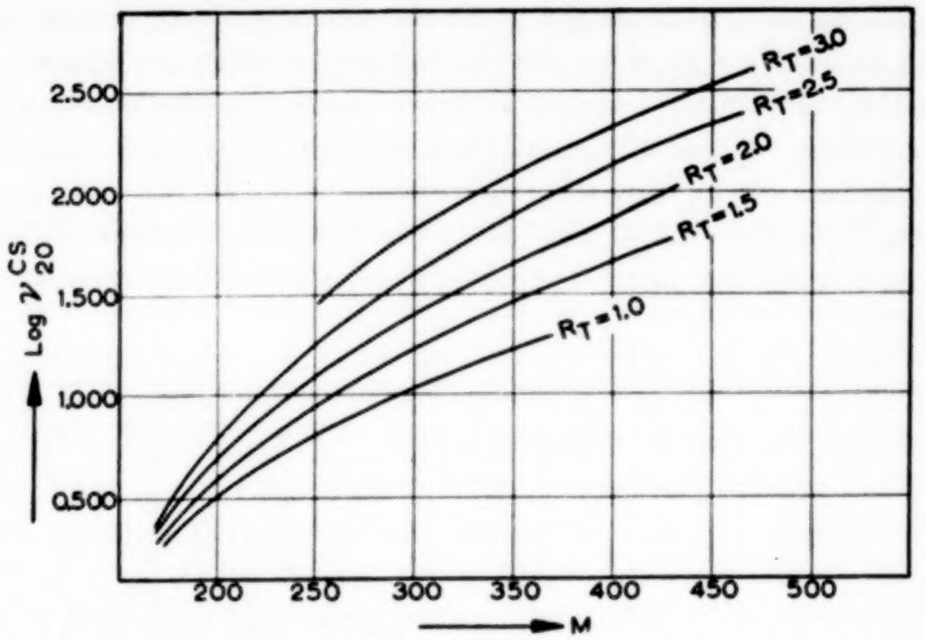


Fig. 12. Log $\nu - M$ diagram for determining the number of rings per molecule in saturated mineral oil fractions.

constructed the diagrams represented in Figs. 11 and 12 for the ring analysis of saturated mineral oil fractions.

With these diagrams it is possible to find the number of (naphthenic) rings per molecule from the molecular weight and kinematic viscosity. However, the accuracy of this determination is in some regions rather small. This is one of the reasons why another diagram[13,14] has been introduced, in which ν_{20}^{cs} has been plotted against the refractive index n_D^{20}, Fig. 13. Another reason is that the molecular weight is preferably not used because its determination is difficult and inaccurate.

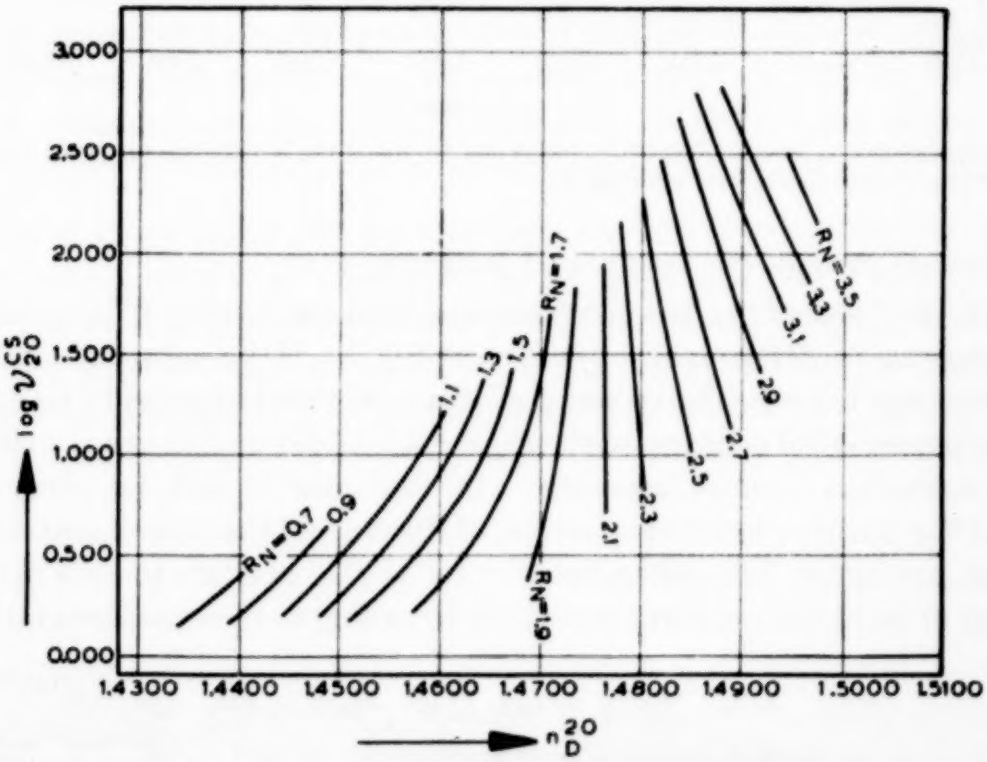


Fig. 13. Log $\nu - n$ diagram for determining the number of rings per molecule in saturated mineral oil fractions.

In Fig. 13 the number of rings per molecule of a saturated mineral oil fraction can be read if the kinematic viscosity and the refractive index are known.

In Fig. 14 the correlation is shown between some physical constants of saturated mineral oil fractions, as well as the relation between physical constants and R_N and $\%C_R$. This diagram shows how the ring-number R_N and the percentage of carbon present in ring structure, $\%C_R$, as well as the molecular weight M and the density d_4^{20}, can be determined for saturated mineral oil fractions by means of their log ν_{20}^{cs} and n_D^{20} values.

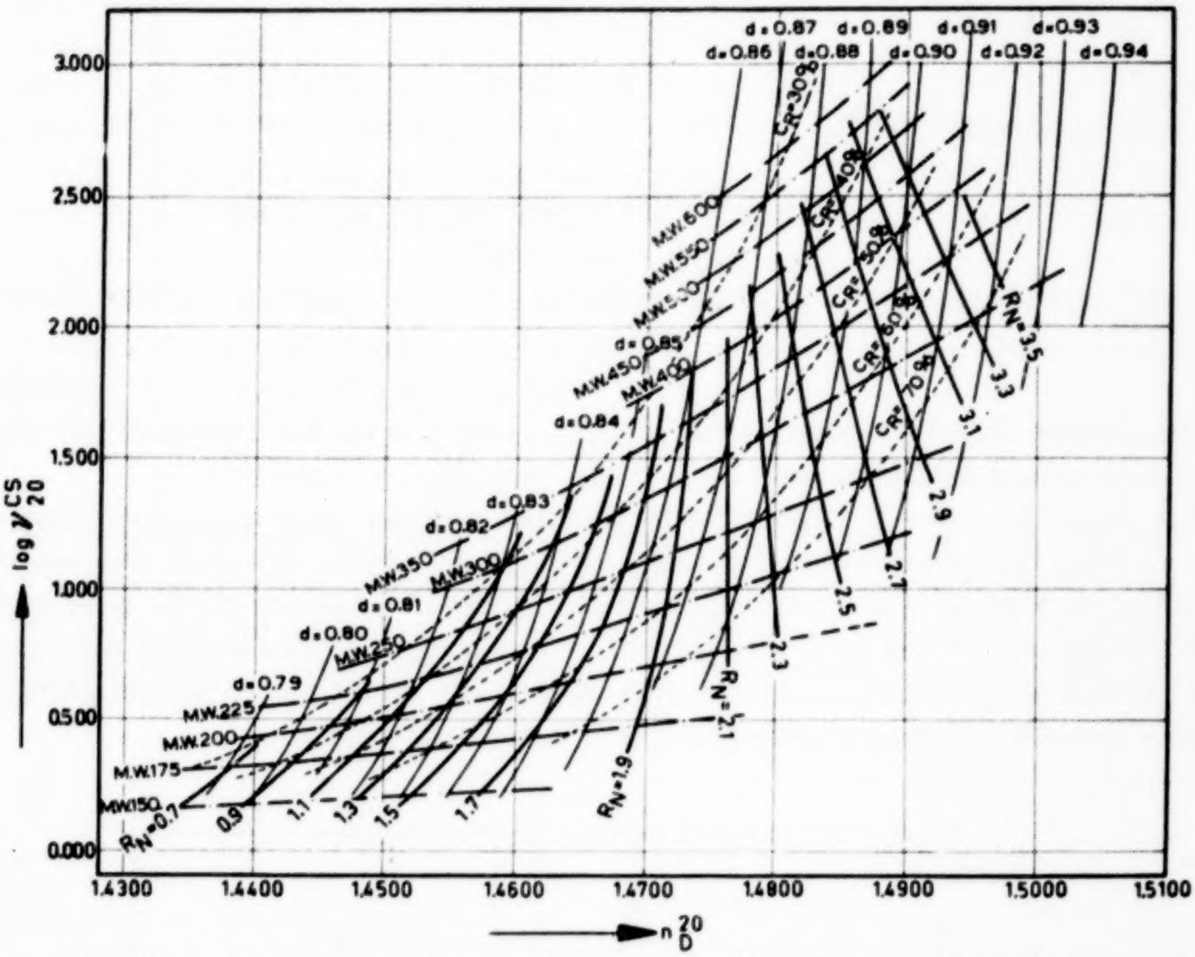


Fig. 14. Correlation of some physical constants of saturated mineral oil fractions; the relation between physical constants and structure.

(*ii*) *Structure of straight-run mineral oil fractions*

(*a*) *The v–n–d method.* As has just been discussed the density d_4^{20} of saturated mineral oil fractions can be determined by means of Fig. 14, if the values of log ν_{20}^{cs} and n_D^{20} of the fractions are known. The value of d_4^{20} thus obtained appears to be in accordance with the experimental value up to the third decimal place. This is not so if the fractions under examination contain aromatics. In that case it will be observed that the value d' of the density obtained by means of Fig. 14 and the experimentally determined value d do not agree. The difference $d' - d = \triangle d$ appears to be a measure for the percentage of carbon in aromatic structure according to the experimentally established equation

$$\%C_A = 600 \triangle d - (40 \triangle d)^2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (40)$$

The value of $\%C_A$ thus obtained is independent of the sulphur content. From $\triangle d$, the value of the density d^* and the logarithm of the viscosity log ν^* of the saturated oil fraction can be predicted by means of the experimentally established equations

$$d^* = d - 0.62 \triangle d - 0.008 \%\mathrm{S} \quad \ldots\ldots\ldots\ldots (41)$$

and

$$\log \nu^* = (1 - 3 \triangle d) \log \nu + \triangle d \quad \ldots\ldots\ldots\ldots (42)$$

When determining d^* a correction for the sulphur content has to be applied, which correction is equal to $-0.008 \%\mathrm{S}$.

By means of the values of d^* and $\log \nu^*$ the following values can be read from Fig. 14, *viz.* the number of rings R_N ($= R_T$), the percentage of carbon in ring structure, $\%\mathrm{C}_R$ and the molecular weight, M. The values of R_T, $\%\mathrm{C}_R$ and M are the same for the non-hydrogenated and the saturated oil fractions if it is assumed that the molecular weight does not change on hydrogenation. This is true if no cracking during hydrogenation has taken place within the limits of accuracy of the molecular weight determination.

The number of aromatic rings follows from the values of $\%\mathrm{C}_A$ and M by applying the equations

if $R_A \geqslant 1$

$$(2\, R_A + 1) = \frac{M \cdot \%\mathrm{C}_A}{2800} \quad \ldots\ldots\ldots\ldots (43)$$

if $R_A \leqslant 1$

$$3\, R_A = \frac{M \cdot \%\mathrm{C}_A}{2800} \quad \ldots\ldots\ldots\ldots (44)$$

Equations (43) and (44) can be derived from equations (35) and (29) respectively, recognizing that, in view of the accuracy of the molecular weight determination ($\pm 5\%$), the denominators may be replaced by M, while the constant value 14.026 in the numerators may be replaced by 14.0 without unduly affecting the accuracy of $\%\mathrm{C}_A$.

For the determination of $\%\mathrm{C}_A$ no sulphur correction need be made.

The method described is known as the ***ν–n–d*** method. It has the advantage that the rather laborious, time-consuming and inaccurate determination of the molecular weight can be avoided, while the viscosity can easily be determined with a relatively high accuracy. Furthermore it is now possible to predict the molecular weight.

(*β*) *The ν–n–d space model and its cross-sections.* It has recently been shown by CORNELISSEN AND WATERMAN[15] that use can be made of a log *ν–n–d* space model to determine the carbon-type composition of oil fractions. The space model consists of the mutually perpendicular coordinates $\log \nu_{20}^{\mathrm{cs}}$, n_{D}^{20} and d_4^{20} (ν_{20}^{cs} is the kinematic viscosity in centistokes at 20°C, n_{D}^{20} is the refractive index for the sodium D-line at 20°C and d_4^{20} is the density in g/ml at 20°C); it is schematically represented in Fig. 15.

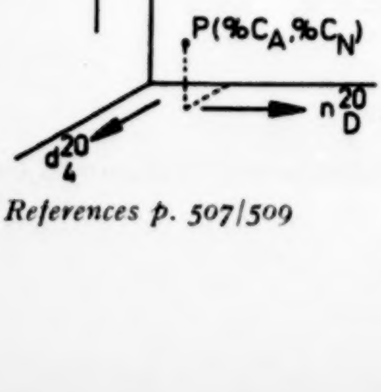


Fig. 15. Schematical representation of the log *ν–n–d* space model for the determination of the carbon-type composition of mineral oil fractions.

In Fig. 15 a fraction P with certain values for log ν_{20}^{cs}, n_D^{20} and d_4^{20} is indicated. The fraction has the assumed composition $\%C_A$ and $\%C_N$. Other fractions with different values of log ν_{20}^{cs}, n_D^{20} and d_4^{20} may have the same carbon-type composition (which is possible if the molecular weights are not the same) or different carbon-type compositions. Fractions with the same carbon type composition form space lines, which are the intersecting lines of surfaces of equal $\%C_A$ and $\%C_N$, respectively.

For practical use of the log $\nu-n-d$ space model, cross-sections are made of these surfaces of equal $\%C_A$ and $\%C_N$ values parallel to the n_D^{20} — d_4^{20} coordinate plane or, in other words, for certain different viscosity values, namely log ν_{20}^{cs} = 0.300, 0.500, 1.000, 1.500, 2.000 and 2.500. The cross-sections are shown in the Figs. 16, 17, 18, 19, 20 and 21, respectively.

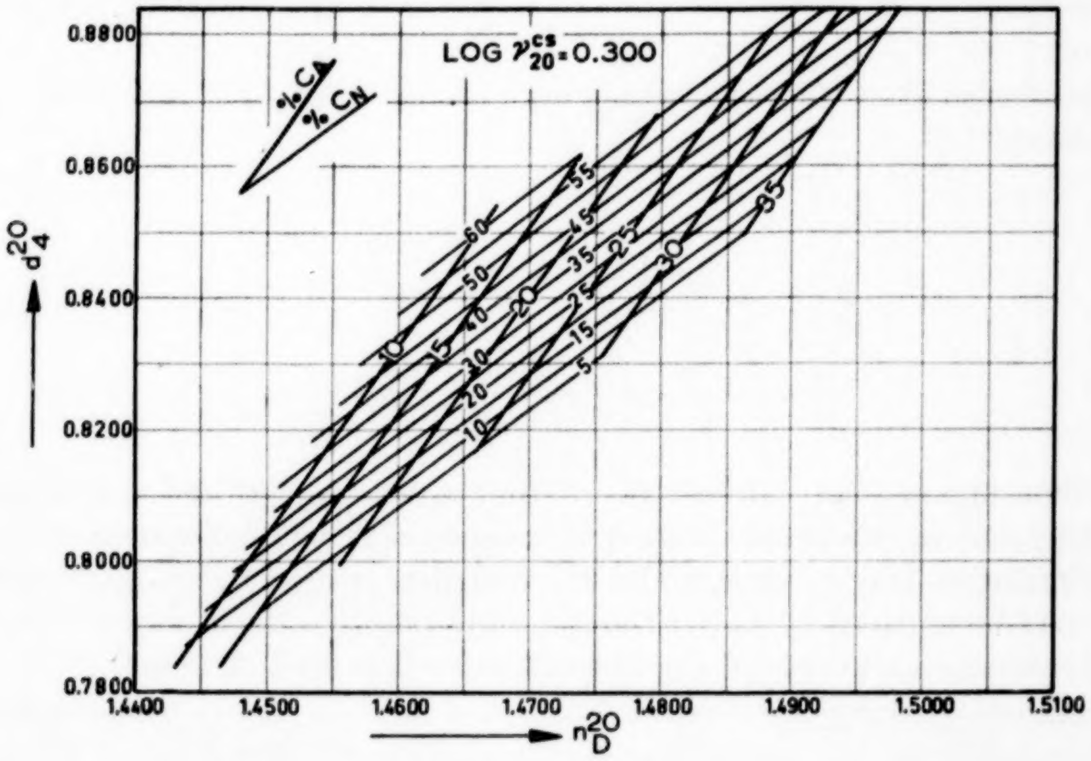


Fig. 16. Cross-section of the log $\nu-n-d$ space model at log ν_{20}^{cs} = 0.300, with the surfaces of equal values of $\%C_A$ and $\%C_N$.

The cross-sections can be used for the determination of the carbon-type composition of mineral oil fractions in the following way.

Example: An oil fraction has the values

$$\log \nu_{20}^{cs} = 0.428$$
$$n_D^{20} = 1.4884$$
$$d_4^{20} = 0.8634$$

As the value of log ν_{20}^{cs} is equal to 0.428 use must be made of the *two* cross-sections for log ν_{20}^{cs} 0.300= and log ν_{20}^{cs} = 0.500, which are the adjacent values of the series of six cross-sections.

In both graphs values of $\%C_A$ and $\%C_N$ are read from the values of n_D^{20} and d_4^{20}; these values are

from the log ν_{20}^{cs} = 0.300 diagram: $\%C_A$ = 32 and
$\%C_N$ = 30

from the log ν_{20}^{cs} = 0.500 diagram: $\%C_A$ = 29 and
$\%C_N$ = 22.

As the real value of log ν_{20}^{cs} of the fraction in question is equal to 0.428, the values of $\%C_A$ and $\%C_N$

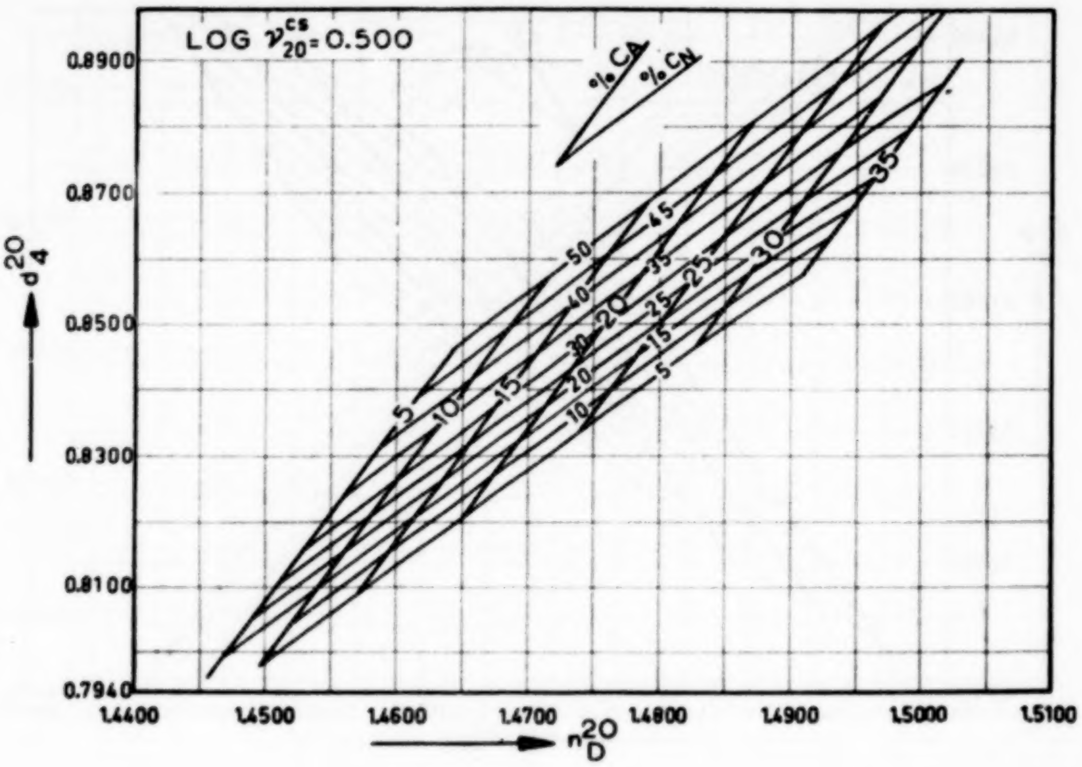


Fig. 17. Cross-section of the log $\nu-n-d$ space model at log ν_{20}^{cs} = 0.500, with surfaces of equal values of %C_A and %C_N.

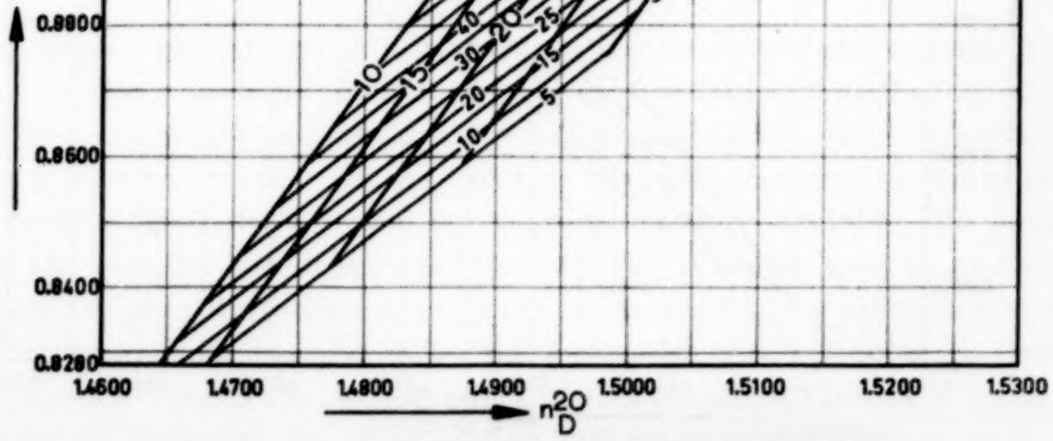


Fig. 18. Cross-section of the log $\nu-n-d$ space model at log ν_{20}^{cs} = 1.000, with surfaces of equal values of %C_A and %C_N.

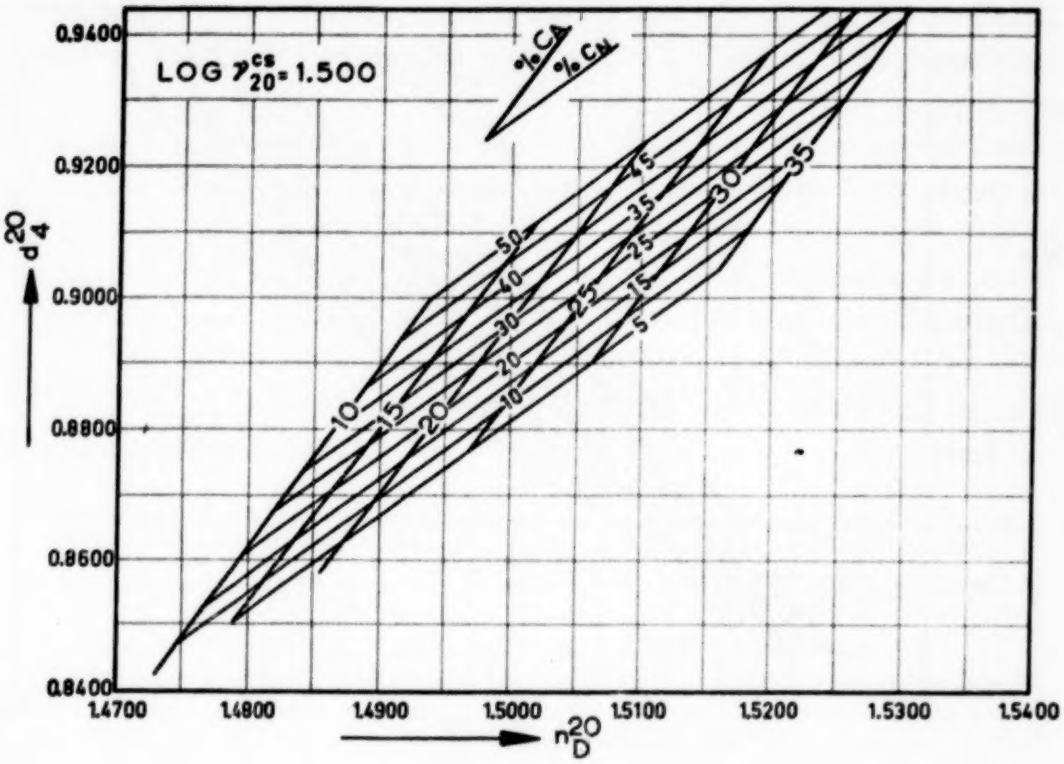


Fig. 19. Cross-section of the log ν–n–d space model at log ν_{20}^{cs} = 1.500, with surfaces of equal values of %C_A and %C_N.

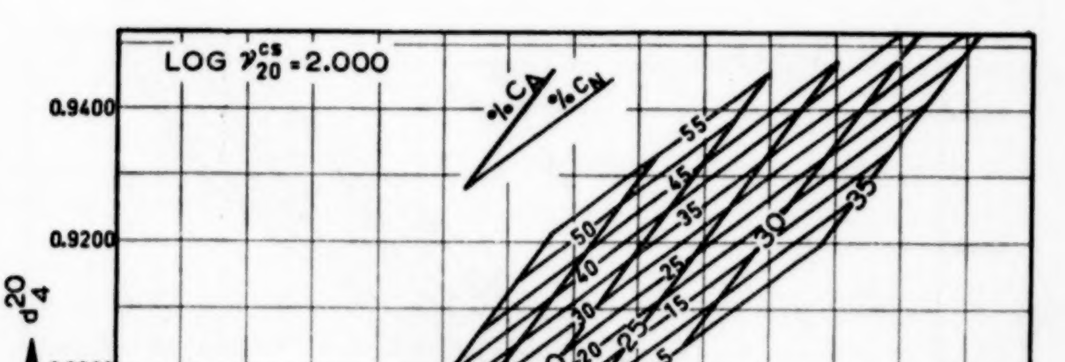


Fig. 20. Cross-section of the log ν–n–d space model at log ν_{20}^{cs} = 2.000, with surfaces of equal values of %C_A and %C_N.

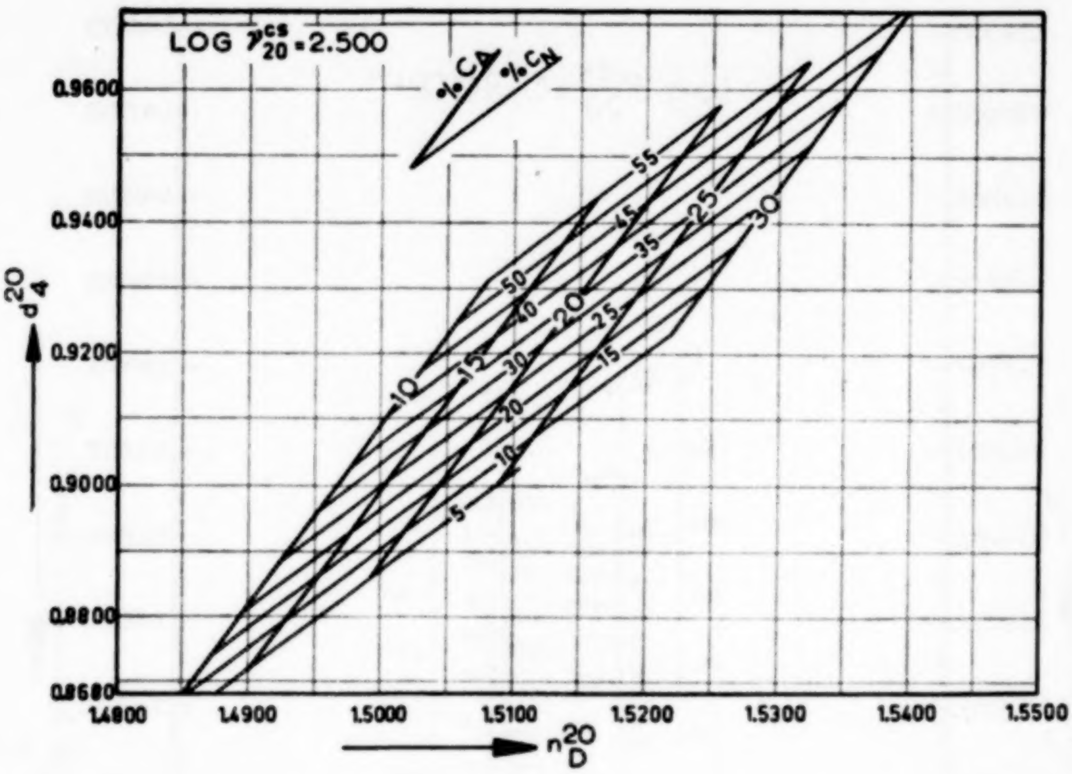


Fig. 21. Cross-section of the log ν–n–d space model at log ν_{20}^{cs} = 2.500, with surfaces of equal values of $\%C_A$ and $\%C_N$.

can be obtained by linear interpolation between the values read from the graphs. The results are

$$\%C_A = 32 - \frac{0.128}{0.200} \cdot 3 = 32 - 2 = 30$$

and

$$\%C_N = 30 - \frac{0.128}{0.200} \cdot 8 = 30 - 5 = 25.$$

The carbon-type composition of the oil appears to be

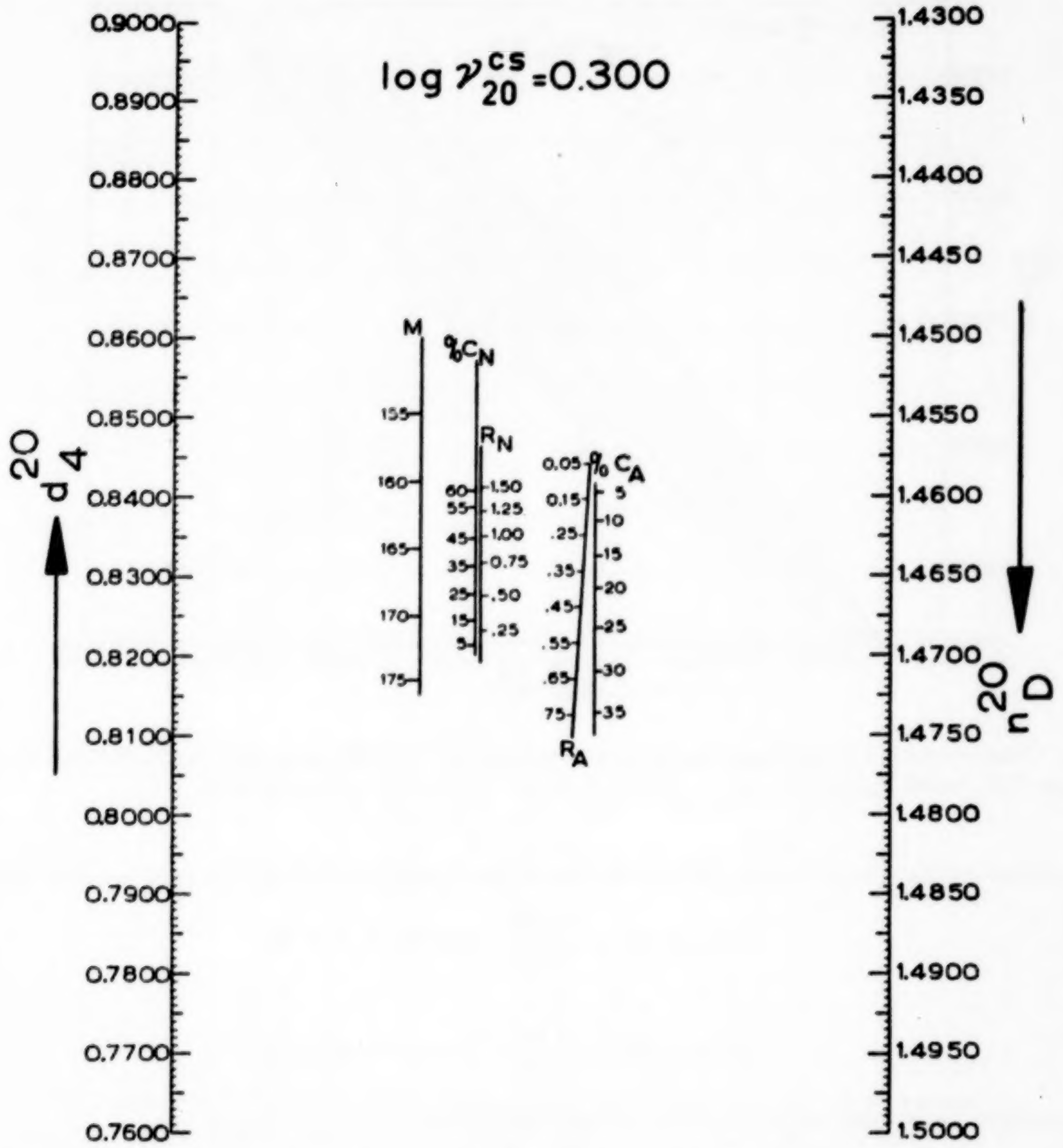
$$\%C_A = 30$$
$$\%C_N = 25$$
$$\%C_P = 45.$$

As no auxiliary constants (like d^* and log ν^*, see preceding section) are used in the log ν–n–d space model cross-section method it can be regarded as an improvement of the application of the viscosity in the field of graphical statistical methods.

(γ) *The application of nomograms of the cross sections of the ν–n–d space model.* A further development of the ν–n–d method is the use of nomograms[16] replacing the cross-sections of the space model, which have been discussed in the previous section. This replacement is possible because the intersecting lines of these cross-sections with the surfaces of equal values of $\%C_A$ and $\%C_N$ are practically straight. If a nomogram is used with the parallel coordinates n_D^{20} and d_4^{20} the straight lines from the cross-sections become single points in the nomogram. As we are dealing with straight *parallel* lines in the cross-sections, the points in the nomogram corresponding to these lines constitute a straight line in the nomogram, which is parallel to both the coordinates.

The nomograms replacing the cross-sections are given in the Figs. 22-27.

In the nomograms not only the lines for the determination of $\%C_A$ and $\%C_N$ are given, but also those for the determination of R_A and R_N as well as molecular weight M.



log ν_{20}^{cs} =0.300
0.9000
0.8900
0.8800
0.8700
0.8600
0.8500
0.8400
0.8300
0.8200
0.8100
0.8000
0.7900
0.7800
0.7700
0.7600
d_4^{20}
M
155
160
165
170
175
%C_N
60
55
45
35
25
15
5
R_N
1.50
1.25
1.00
0.75
.50
.25
%C_A
5
10
15
20
25
30
35
0.05
0.15
.25
.35
.45
.55
.65
75
R_A
1.4300
1.4350
1.4400
1.4450
1.4500
1.4550
1.4600
1.4650
1.4700
1.4750
1.4800
1.4850
1.4900
1.4950
1.5000
n_D^{20}

Fig. 22. Nomogram of the cross-section of the log $\nu - n - d$ space model at log $\nu_{20}^{cs} = 0.300$.

The use of the nomograms will be illustrated by an example.

Example: An oil fraction has the values

$$\begin{aligned} \log \nu_{20}^{cs} &= 0.828 \\ n_D^{20} &= 1.4695 \\ d_4^{20} &= 0.8390 \\ M &= 232 \end{aligned}$$

As the value of log ν_{20}^{cs} is equal to 0.828 use has to be made of the two nomograms for log ν_{20}^{cs} = 0.500 and log ν_{20}^{cs} = 1.000, these being the adjacent values of the six cross-sections. In these two nomograms the following values of %C_A, %C_N, R_A, R_N and M are read from the values of n_D^{20} and d_4^{20}.

nomogram	%C_A	%C_N	R_A	R_N	M
log ν_{20}^{cs} = 0.500	17	29	0.39	0.71	191
log ν_{20}^{cs} = 1.000	12	18	0.40	0.74	262

As the value of log ν_{20}^{cs} of the fraction in question is equal to 0.828 the values of %C_A, %C_N, R_A, R_N and M can be obtained by linear interpolation between the values read from the graph. The results are

$$\%C_A = 17 - \frac{0.328}{0.500} \cdot 5 = 17 - 3 = 14$$

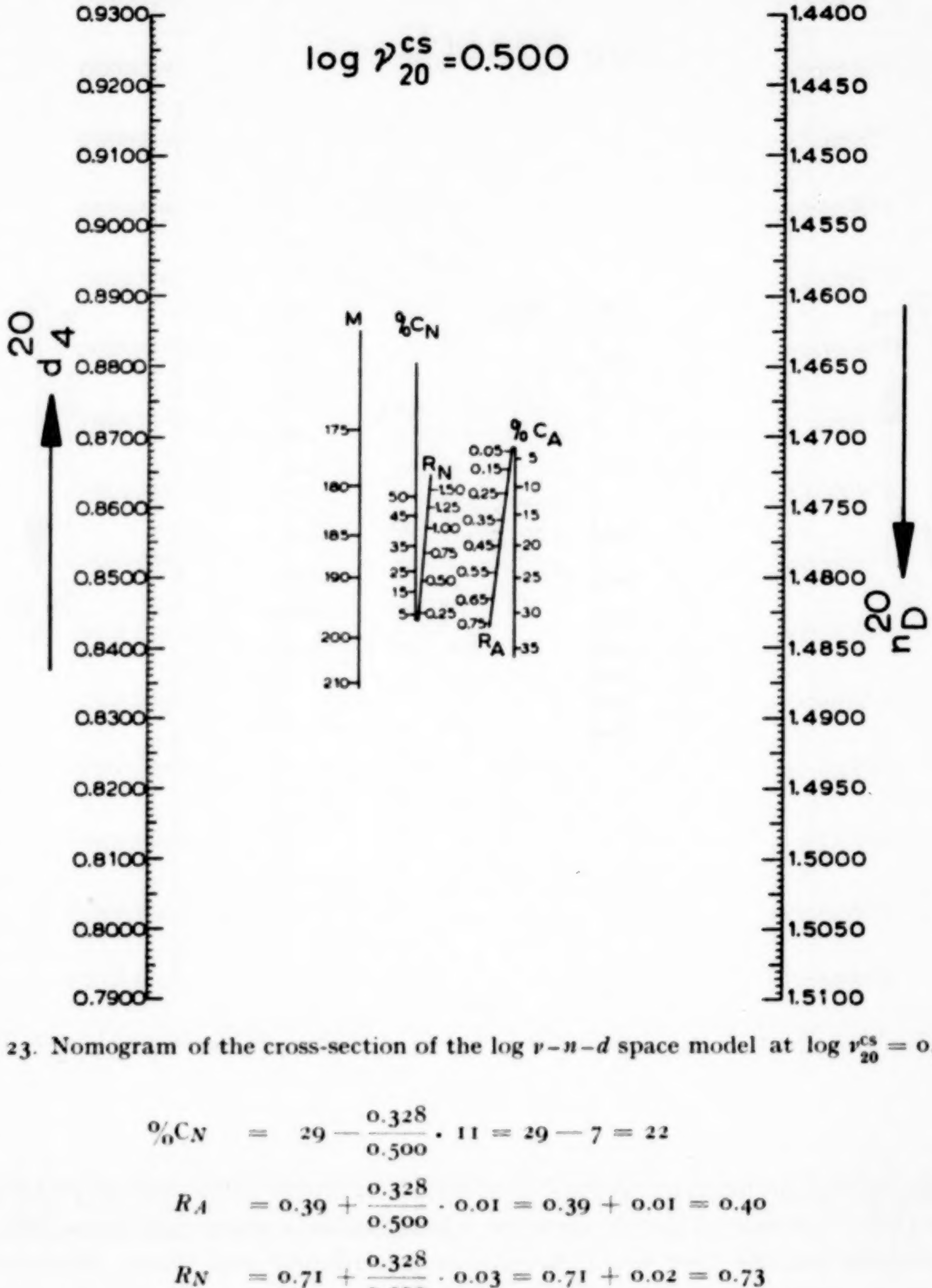


Fig. 23. Nomogram of the cross-section of the log $\nu - n - d$ space model at log $\nu^{cs}_{20} = 0.500$.

$$\%C_N = 29 - \frac{0.328}{0.500} \cdot 11 = 29 - 7 = 22$$

$$R_A = 0.39 + \frac{0.328}{0.500} \cdot 0.01 = 0.39 + 0.01 = 0.40$$

$$R_N = 0.71 + \frac{0.328}{0.500} \cdot 0.03 = 0.71 + 0.02 = 0.73$$

$$\text{and } M = 191 + \frac{0.328}{0.500} \cdot 71 = 191 + 47 = 238$$

It appears that the different structural elements and molecular weight have the following values:

$\%C_A = 14$	$R_A = 0.40$
$\%C_N = 22$	$R_N = 0.73$
$\%C_R = 36$	$R_T = 1.13$
$\%C_P = 64$	$M = 238$

It must be emphasized that the nomograms and cross-sections presented here are only applicable to the original mineral oil fractions and not to the hydrogenated fractions. The advantage of using the nomograms instead of the cross-sections lies in the

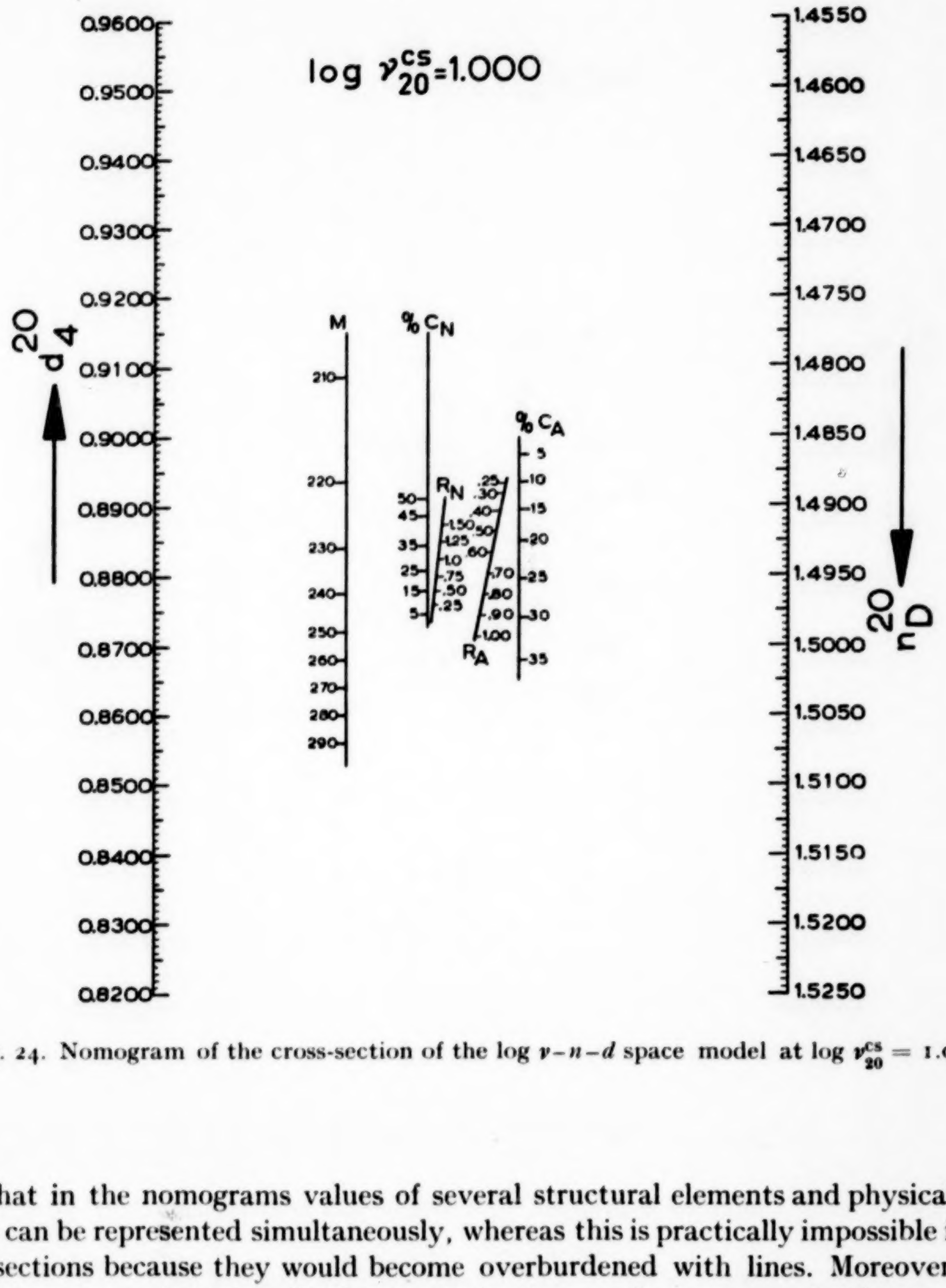

log ν_{20}^{cs}=1.000
0.9600
0.9500
0.9400
0.9300
0.9200
0.9100
0.9000
0.8900
0.8800
0.8700
0.8600
0.8500
0.8400
0.8300
0.8200
d_4^{20}
M
210
220
230
240
250
260
270
280
290
%C_N
50
45
35
25
15
5
R_N
1.50
1.25
1.0
.75
.50
.25
.25
.30
.40
.50
.60
.70
.80
.90
1.00
R_A
%C_A
5
10
15
20
25
30
35
1.4550
1.4600
1.4650
1.4700
1.4750
1.4800
1.4850
1.4900
1.4950
1.5000
1.5050
1.5100
1.5150
1.5200
1.5250
n_D^{20}

Fig. 24. Nomogram of the cross-section of the log $\nu-n-d$ space model at log ν_{20}^{cs} = 1.000.

fact that in the nomograms values of several structural elements and physical constants can be represented simultaneously, whereas this is practically impossible in the cross-sections because they would become overburdened with lines. Moreover, the nomograms are easier to handle. Consequently they can be recommended for practical use for making the carbon-type analysis and ring analysis of mineral oil fractions.

(δ) *The applications of log ν-f(n, d) graphs.* It may sometimes be felt as a drawback that the methods described under (β) and (γ) require the use of *two* different cross-sections or nomograms. If one wishes to know, for instance, the value of one structural element, say %C_A, it proves to be possible to construct a graph from which %C_A can be read directly. The graph has as coordinates log ν_{20}^{cs} and a simple function of the refractive index and the density. Two such graphs have been constructed by CORNELISSEN AND WATERMAN[17], one for the determination of %C_A and one for the determination of %C_N (Figs. 28 and 29, respectively).

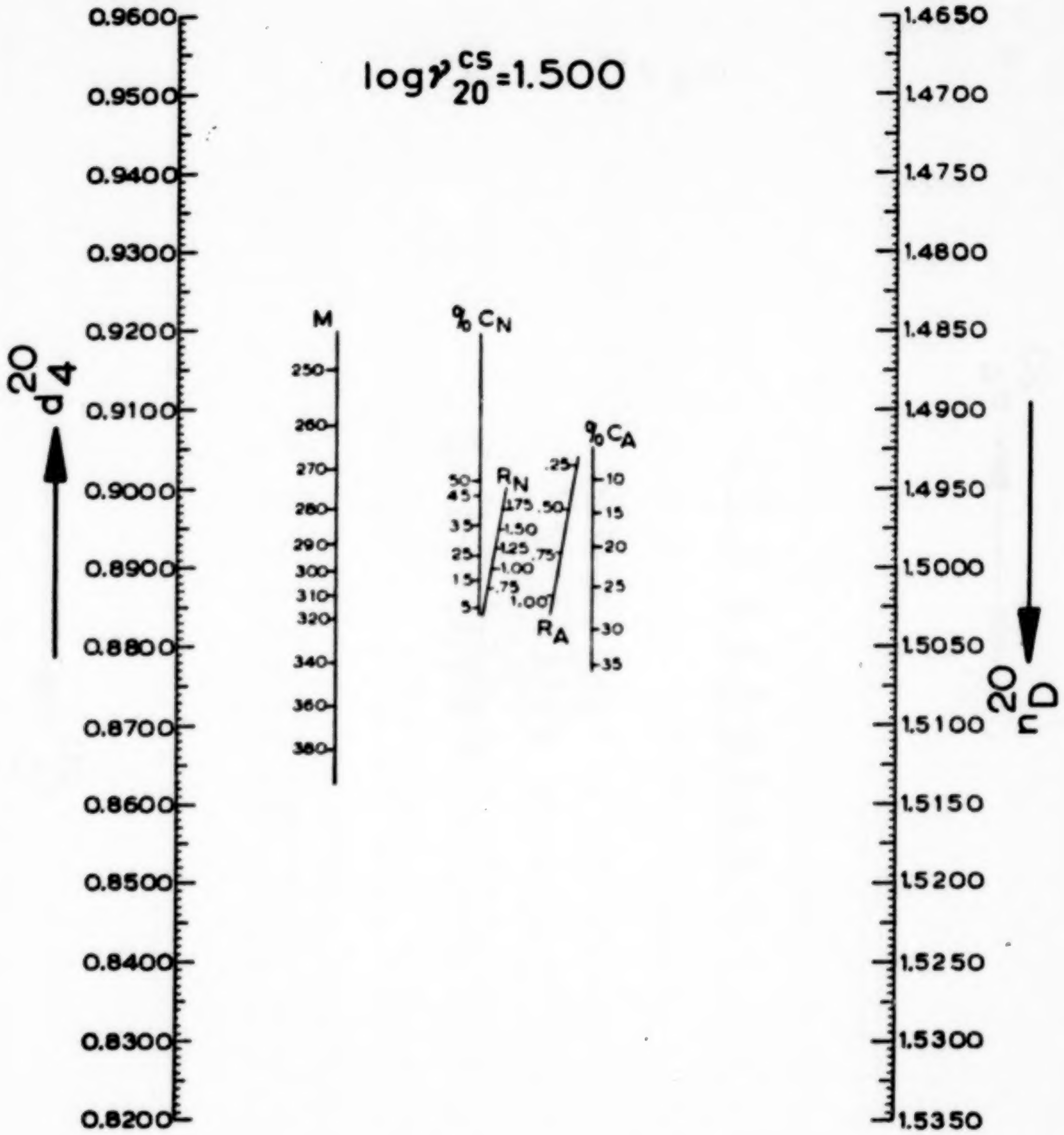


Fig. 25. Nomogram of the cross-section of the log $\nu-n-d$ space model at log ν^{cs}_{20} = 1.500.

These graphs can be derived from the cross-sections of the log $\nu-n-d$ space model. In these cross-sections the lines of equal values of $\%C_A$ and $\%\,C_N$ have a constant slope. Accordingly the general equation of these lines can be represented by

$$n^{20}_{\mathrm{D}} = a \cdot d^{20}_{4} + b$$

in which a is a constant, whereas the value of b varies.

Since

$$b = n^{20}_{\mathrm{D}} - a \cdot d^{20}_{4}$$

it follows that b, or $n^{20}_{\mathrm{D}} - a \cdot d^{20}_{4}$, represents a certain value of $\%C_A$ or $\%C_N$ for the constant value of log ν of the considered cross-section.

In the log $\nu-b(= n - a \cdot d)$ graphs the lines of equal values of $\%C_A$ and $\%C_N$ from the cross-sections for a certain viscosity, are represented by points lying on a line parallel to the $n - a \cdot d$ axis.

When the points for the different log ν values of the respective cross-sections are connected, lines are obtained as given in Figs. 28 and 29.

The value of a is equal to the cotangent of the slope of the lines of equal $\%C_A$ or $\%C_R$ in the cross-sections of the log $\nu-n-d$ space-model.

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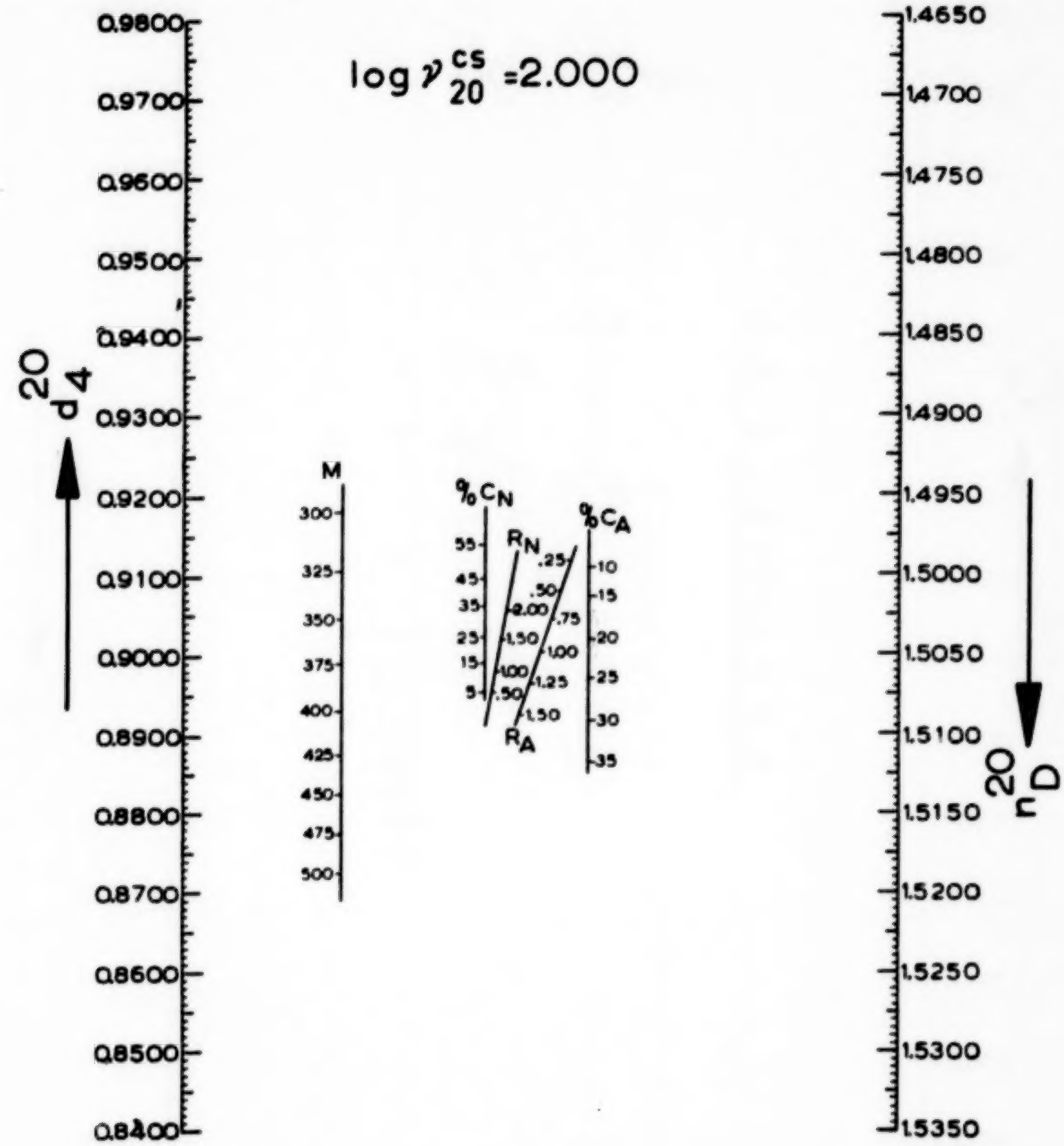

Fig. 26. Nomogram of the cross-section of the log $\nu-n-d$ space model at log $\nu_{20}^{cs} = 2.000$.

The function of the refractive index and the density in the case of the determination of %C_A proves to be $(n—0.35d)$ and in the case of the determination of %C_N $(n - {}^2/_3\, d)$.

The use of the graphs does not need further explanation. The value of the coefficients of d in the (n,d) functions have been derived from the constant slope of the lines of equal values of %C_A and %C_N in the cross-sections.

Though these graphs are convenient to use it is a drawback that for each structural element a different graph has to be employed. Therefore the nomogram method in general seems to be the most attractive method for determining the values of the various structural elements of mineral oil fractions.

3. CORRELATION OF PHYSICAL CONSTANTS OF MINERAL OIL FRACTIONS

In this section it will be shown that it is not only possible to determine the chemical structure of mineral oil fractions from physical constants, but also to predict the values of other physical constants. That it is possible to correlate the physical constants of

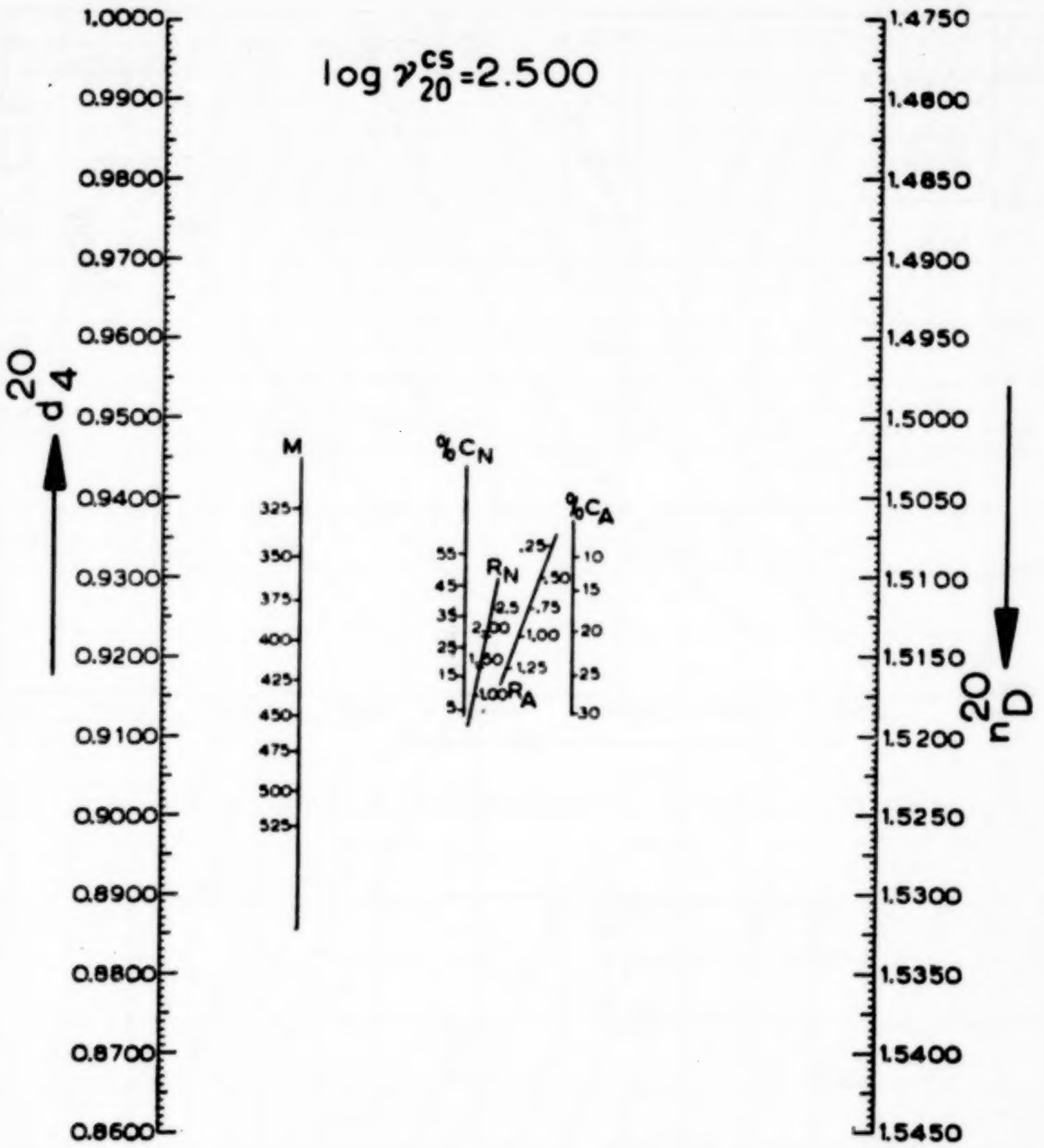

Fig. 27. Nomogram of the cross-section of the log ν–n–d space model at log ν_{20}^{cs} = 2.500.

saturated mineral oil fractions can be seen from a few particular examples, previously given in connection with the determination of %C_N.

These are:

(a) The correlation between specific refraction, molecular weight and aniline point or density (p. 414, Figs. 9 and 10).

(b) The correlation between kinematic viscosity, refractive index and density (p. 422, Fig. 14)

New methods of finding correlations between physical constants of straight-run as well as of saturated mineral oil fractions will be discussed below.

a. Correlation of the viscosity, the refractive index, the density and the ultrasonic sound velocity of mineral oil fractions

(*i*) *Application of cross-sections of the log ν–n–d space model*

It has been found by CORNELISSEN AND WATERMAN[18] that it is possible to construct surfaces of equal values of the ultrasonic sound velocity in the log ν–n–d space model.

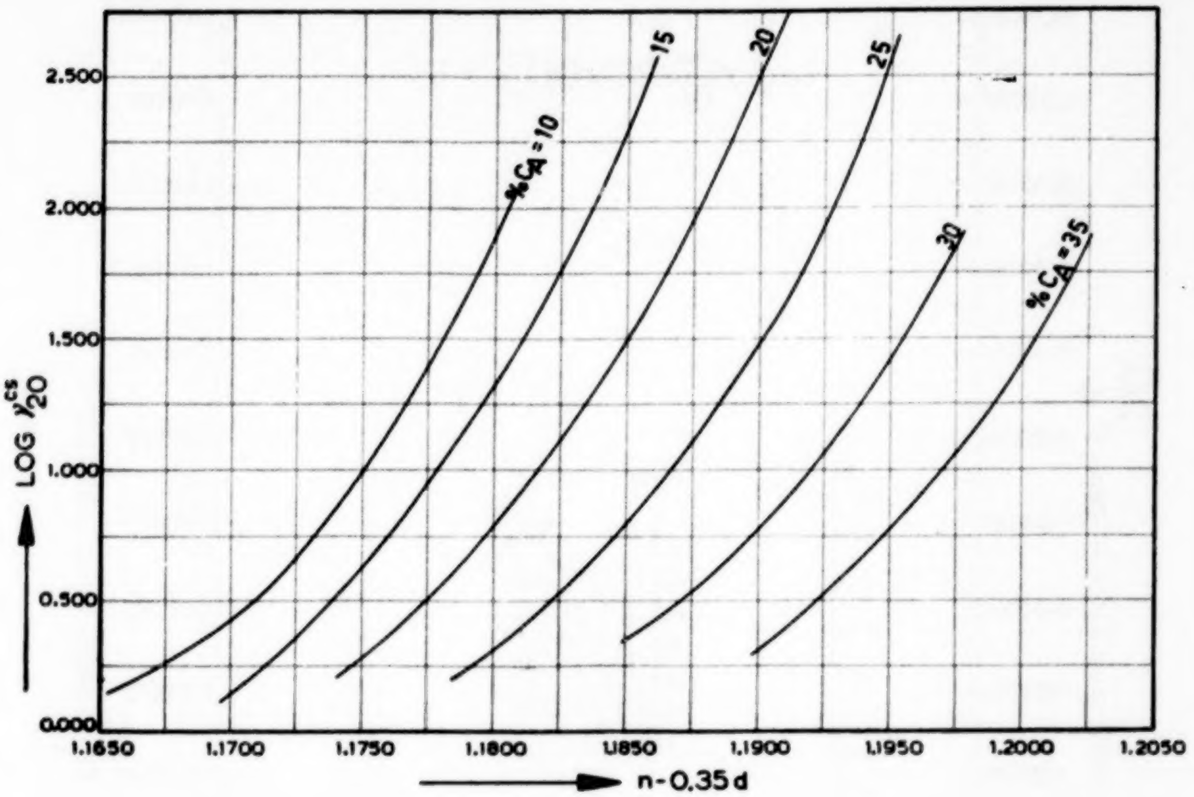

Fig. 28. Log ν_{20}^{cs}-(n—0.35d) graph for the determination of %C_A in mineral oil fractions.

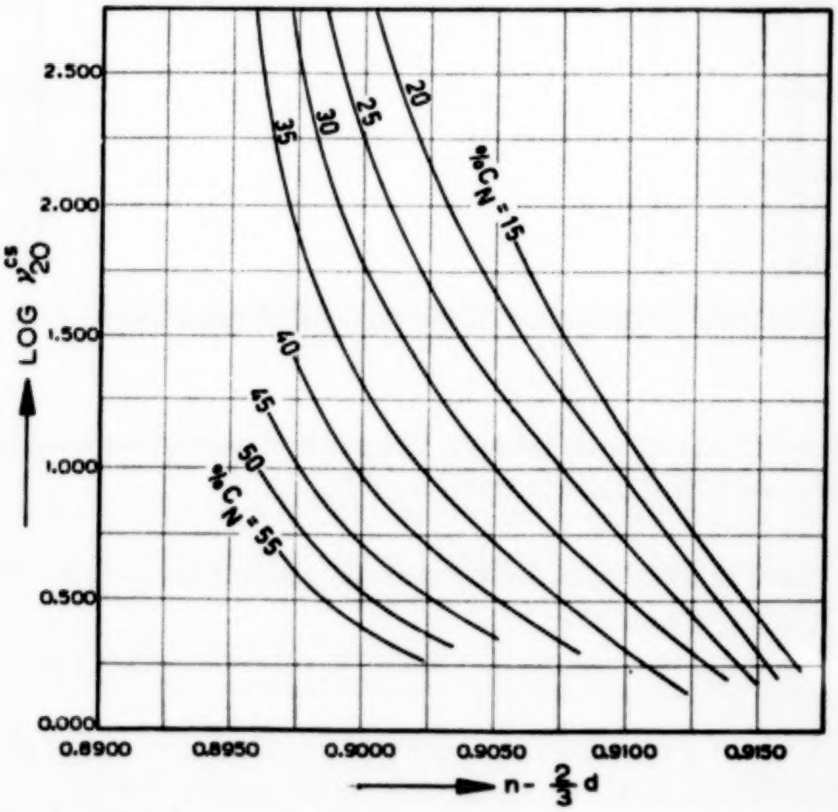

Fig. 29. Log ν_{20}^{cs}-(n—2/3d) graph for the determination of %C_N in mineral oil fractions.

For practical purposes it is necessary to represent the connection between the ultrasonic sound velocity u (m/sec) and ν, n and d by means of cross-sections for constant log ν values of the log ν-n-d space model. The sections contain the intersecting lines with the surfaces of equal u values, Figs. 30, 31, 32, 33 and 34.

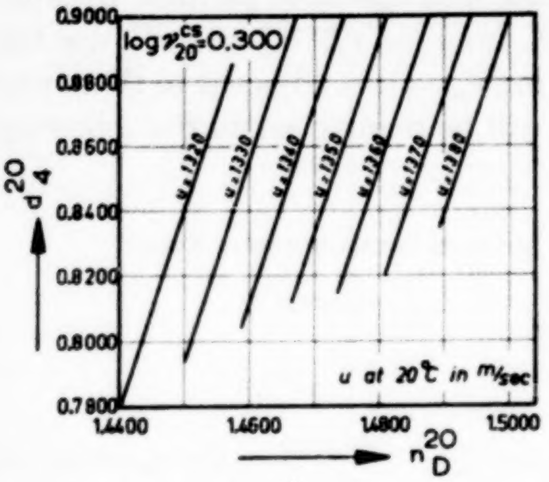

Fig. 30. Cross-section of the log $\nu-n-d$ space model at log ν_{20}^{cs} = 0.300.

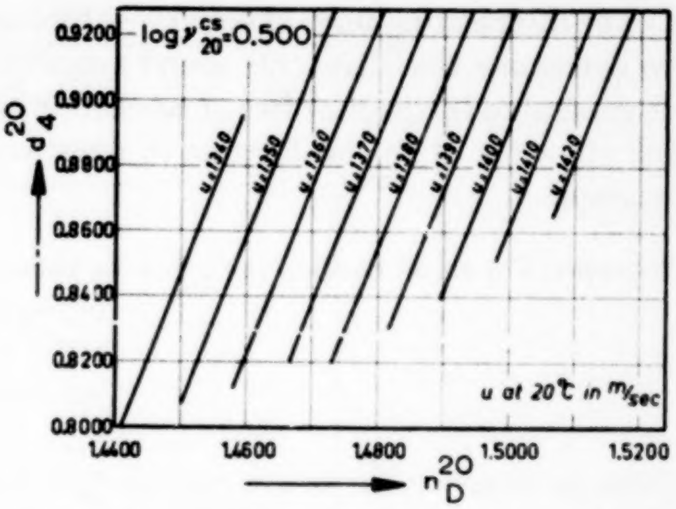

Fig. 31. Cross-section of the log $\nu-n-d$ space model at log ν_{20}^{cs} = 0.500.

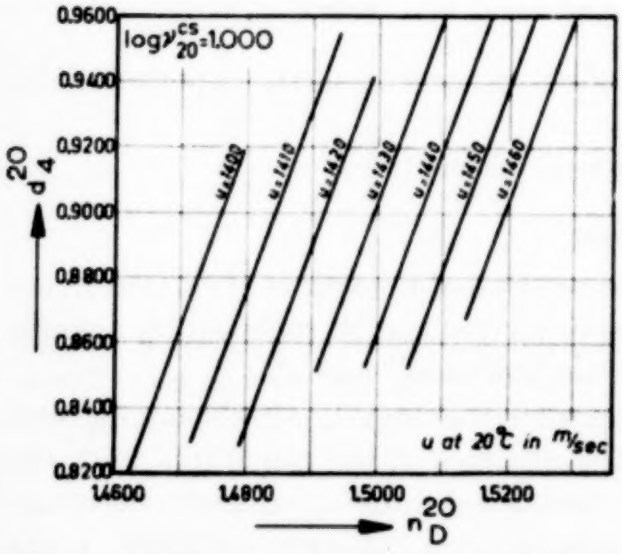

Fig. 32. Cross-section of the log $\nu-n-d$ space model at log ν_{20}^{cs} = 1.000.

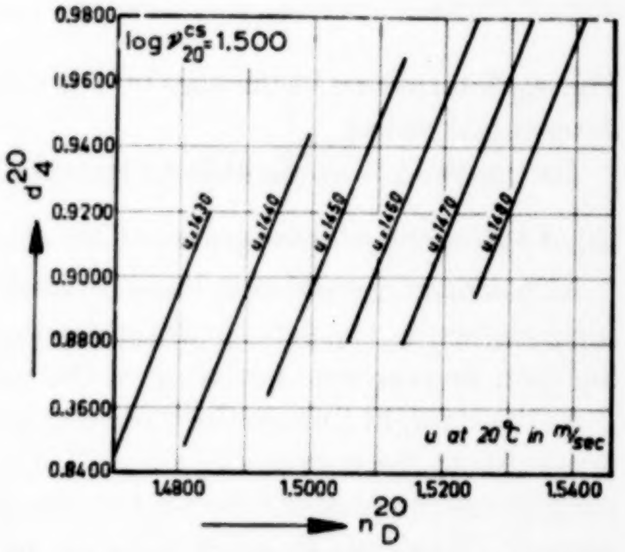

Fig. 33. Cross-section of the log $\nu-n-d$ space model at log ν_{20}^{cs} = 1.500.

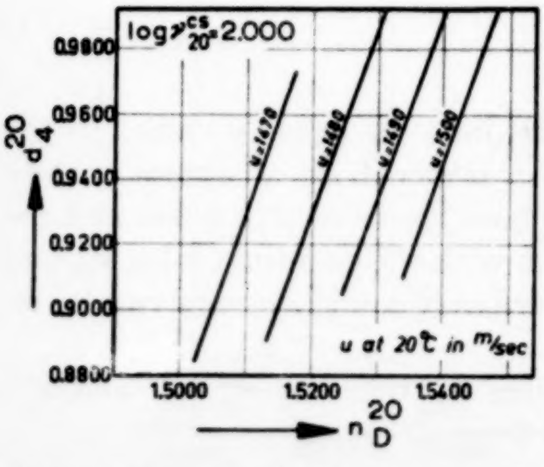

Fig. 34. Cross-section of the log $\nu-n-d$ space model at log ν_{20}^{cs} = 2.000.

The figures 30–34 are related to mineral oil fractions.

The intersecting lines of equal u values are straight and mutually parallel. In order to determine the ultrasonic sound velocity at 20°C from log ν_{20}^{cs}, n_D^{20} and d_4^{20}, use has in general to be made of two cross-sections for the log ν_{20}^{cs} values adjacent to the actual log ν_{20}^{cs} value of the oil fraction in question. This will be made clear in the following example.

Example: For an oil fraction the following values of the physical constants were found:

$$\begin{aligned} \log \nu_{20}^{cs} &= 0.828 \\ n_D^{20} &= 1.4695 \\ d_4^{20} &= 0.8390 \\ u_{20} &= 1394 \text{ m/sec} \end{aligned}$$

From the cross-sections for constant log $\nu_{20}^{cs} = 0.500$ and log $\nu_{20}^{cs} = 1.000$ values, the u_{20} values are read by means of the values $n_D^{20} = 1.4695$ and $d_4^{20} = 0.8390$: $u_{20} = 1369$ m/sec and 1405 m/sec respectively.

By linear interpolation the following value is obtained:

$$u_{20} = 1369 + \frac{0.328}{0.500} \cdot 36 = 1369 + 24 = 1393.$$

$u_{20} = 1393$ m/sec, while the experimental value amounted to 1394 m/sec, measured at a frequency of $2 \cdot 10^6$ Hertz.

The u_{20} determined in the way just described is about as accurate as the experimentally determined value.

The method is applicable to the original mineral oil fractions.

(*ii*) *Application of nomograms of the cross-sections*

As has been discussed in the case of the determination of the values of certain structural elements, the sets of straight lines in a cross-section can be replaced by a single line in a nomogram consisting of the parallel coordinates n_D^{20} and d_4^{20}.

As the straight lines in the cross-sections are parallel, the single line in the nomograms is parallel to the coordinate axes n_D^{20} and d_4^{20}. The distance of the single line from the parallel coordinates will depend on the slope of the lines of equal u_{20} values in the cross-sections. Since the slope of the lines in the cross-sections amounts to about 3, the situation of the single line in the nomogram is as represented in Fig. 35, provided that the scales in both the cross-section and the nomogram are the same.

The way in which u_{20} can be determined from log ν_{20}^{cs}, n_D^{20} and d_4^{20} by means of the nomogram is the same as described for the cross-sections in the preceding section and will not further be discussed.

(*iii*) *Application of a log* ν*-*$(n - \frac{1}{6} d)$ *graph*

As has already been discussed, the slopes of the lines for equal u values in the cross-sections for constant log ν values of the log ν-n-d model, are all approximately the same, provided the same scales are chosen for both the refractive index and the density. Therefore it is possible to construct a graph with the coordinates log ν_{20}^{cs} and $(n - \frac{1}{6} d)$, in which lines of equal values of the ultrasonic sound velocity can be indicated[19]. This has been done in Fig. 36.

By means of this graph it is possible to determine u_{20} from log ν_{20}^{cs}, n_D^{20} and d_4^{20}, if the value of the function $(n - \frac{1}{6} d)$ is calculated from n_D^{20} and d_4^{20}.

It appears that the lines of equal values of the ultrasonic sound velocity in the graph are straight. The slope of the lines changes steadily from one line to the next.

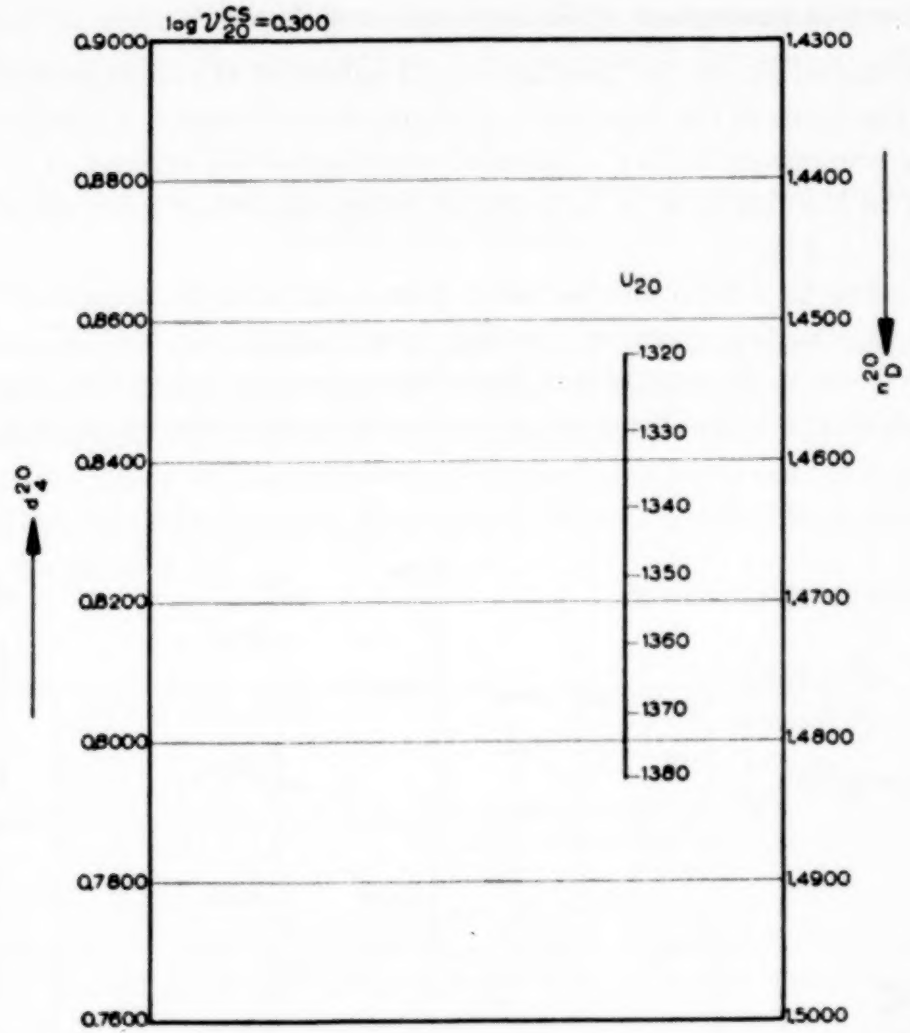

Fig. 35. Nomogram for the determination of u_{20}, replacing a cross-section of the log $\nu-n-d$ space model at $\log \nu^{cs}_{20} = 0.300$.

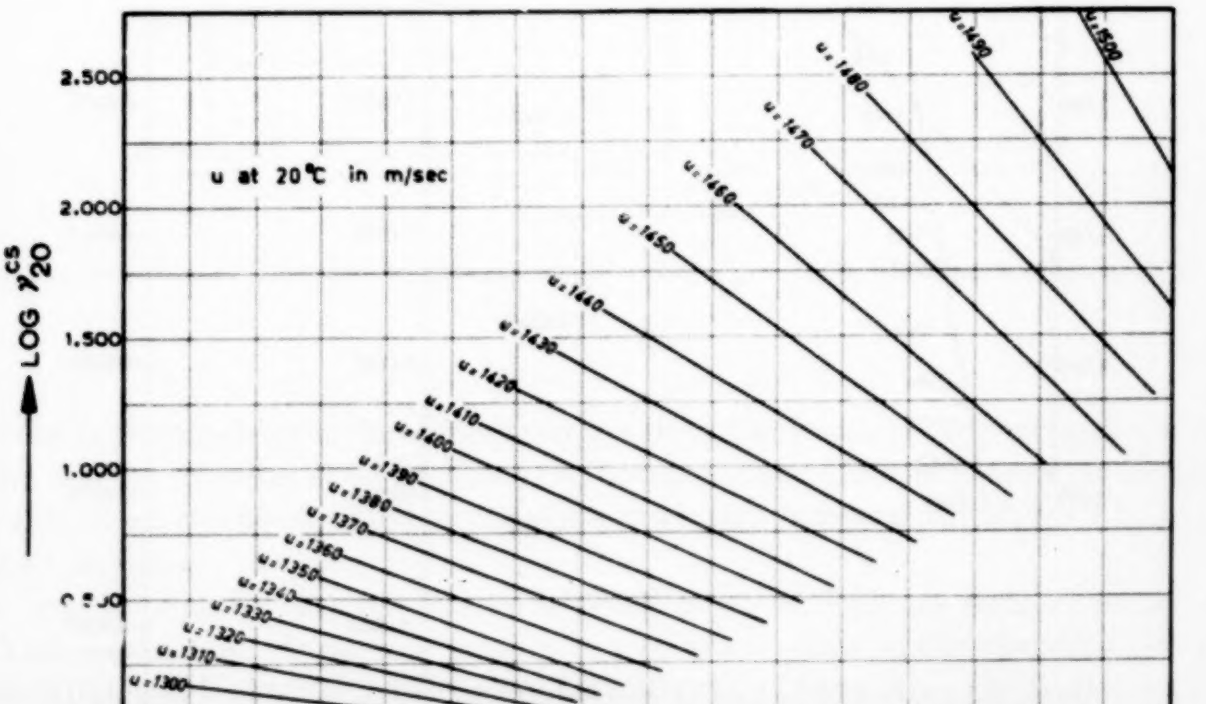

Fig. 36. Log $\nu-(n - \frac{1}{6}\,d)$ graph for the determination of u of mineral oil fractions.

(iv) Application of a nomogram of the log ν *-(*$n - \frac{1}{6}d$*) graph*

As has been stated above the lines for equal values of the ultrasonic sound velocity of mineral oil fractions in the log ν-($n - \frac{1}{6}d$) graph are straight. Therefore it is possible to construct a nomogram with the parallel coordinates log ν_{20}^{cs} and (n — 0.181 d), the value of 0.181 in the function (n — 0.181 d) being somewhat more accurate than $\frac{1}{6}$ in the function ($n - \frac{1}{6}d$).

It is also possible to determine the value of (n — 0.181 d) by means of the nomogram given in Fig. 37. For this purpose parallel coordinates n_D^{20} and d_4^{20} parallel to the log ν_{20}^{cs} and (n — 0.181 d) coordinates have been constructed in the appropriate way.

In Fig. 37 an example has been given how to determine the value of u_{20} from log ν_{20}^{cs},

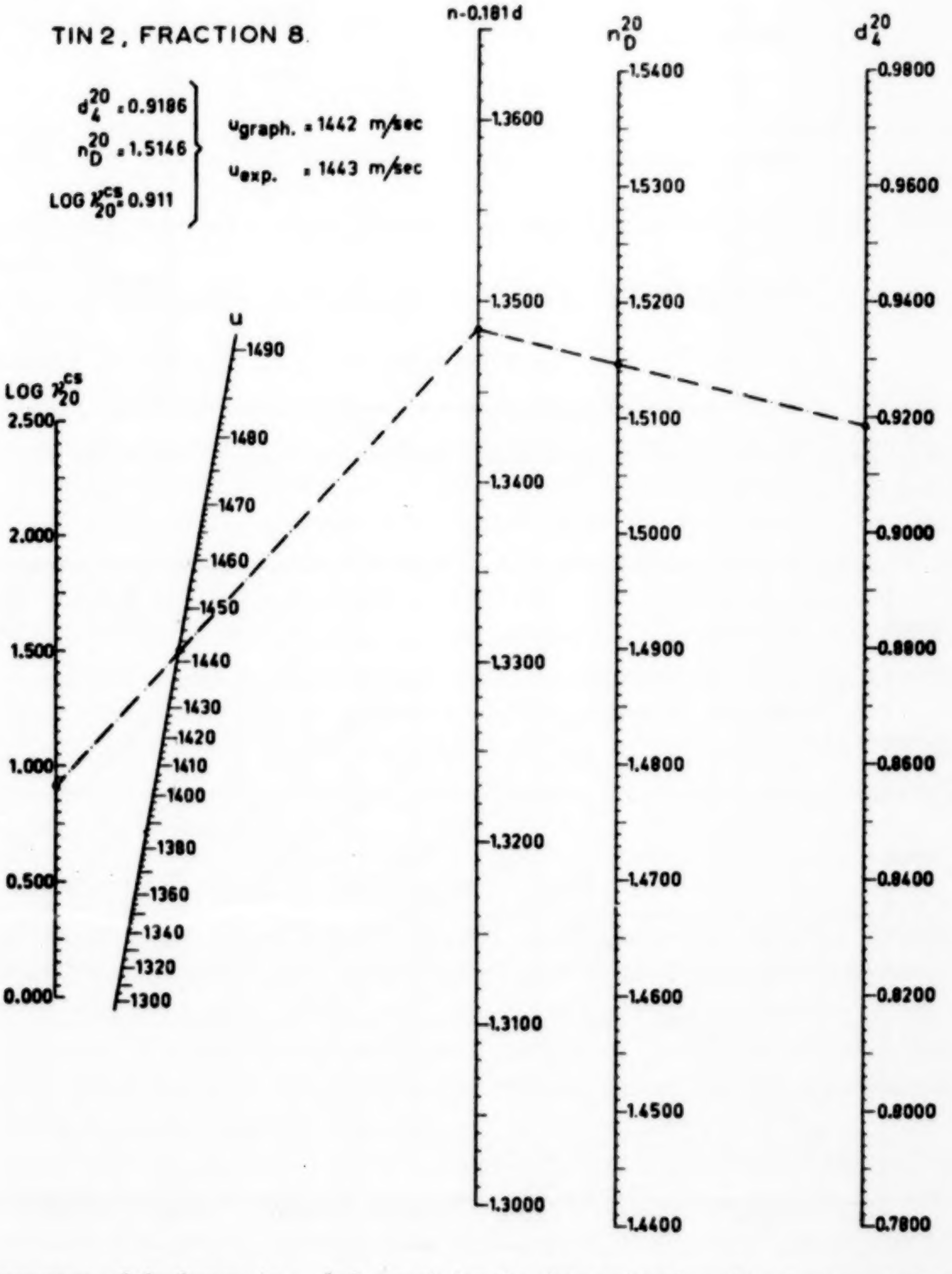

Fig. 37. Nomogram of the log ν-($n - \frac{1}{6}d$) graph for the determination of u of mineral oil fractions.

d_4^{20} and n_D^{20} by means of the nomogram. The use of the nomogram is more attractive than the use of the graph (Fig. 36) since no calculations of the $(n - d)$ function have to be made.

b. Correlation of the viscosity, the refractive index, the density and the surface tension of mineral oil fractions

(i) Application of cross-sections of the v-n-d *space model*

It is possible to construct surfaces of equal values of the surface tension σ in the log v-n-d space model in the same way as surfaces of equal values of $\%C_A$ and $\%C_N$ and the ultrasonic sound velocity have been constructed before. For practical application use has to be made of five different cross-sections for constant log v-values, as has been worked out by CORNELISSEN, HARVA AND WATERMAN[20]. These are represented in Figs. 38, 39, 40, 41 and 42.

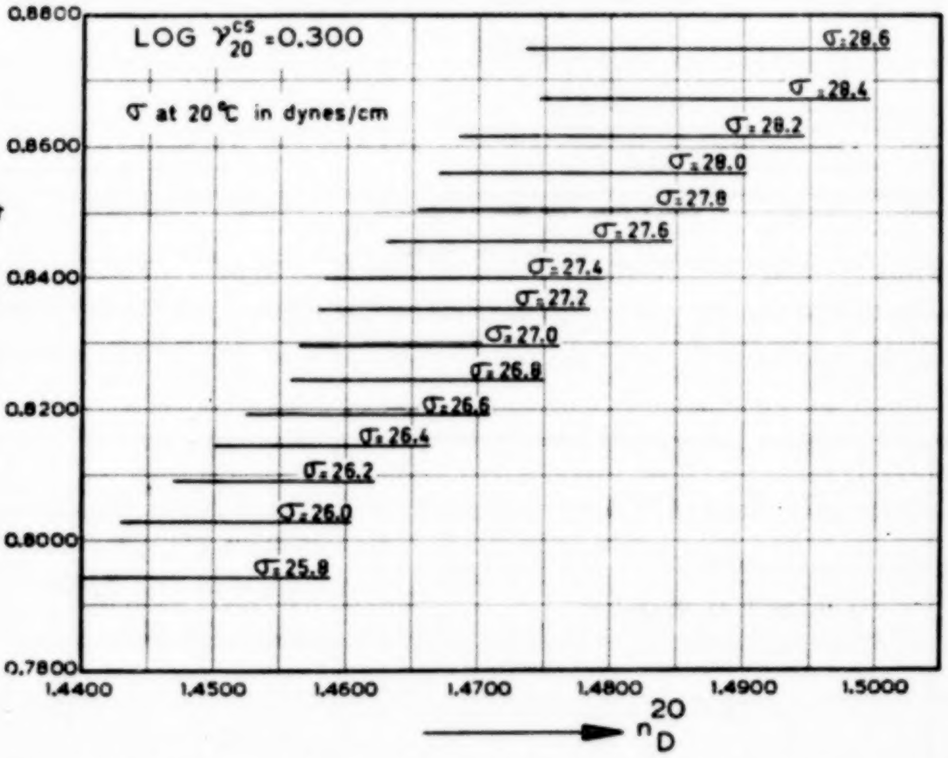

Fig. 38. Cross-section of the log ν-n-d space model at log $\nu_{20}^{cs} = 0.300$, for the determination of σ_{20}.

For the determination of the surface tension from the viscosity, the refractive index and the density of mineral oil fractions two cross-sections have, in general, to be used. The value of σ_{20} can be obtained by linear interpolation between values read from the two cross-sections.

The lines for equal values of σ in the different cross-sections are parallel to the n_D^{20} axis. This means that the surface tension at a constant value of the viscosity and the density is independent of the refractive index and in fact of any other physical constant, *i.e.* the viscosity and the density are the only two physical constants of mineral oil fractions that are necessary to determine the value of the surface tension of these fractions.

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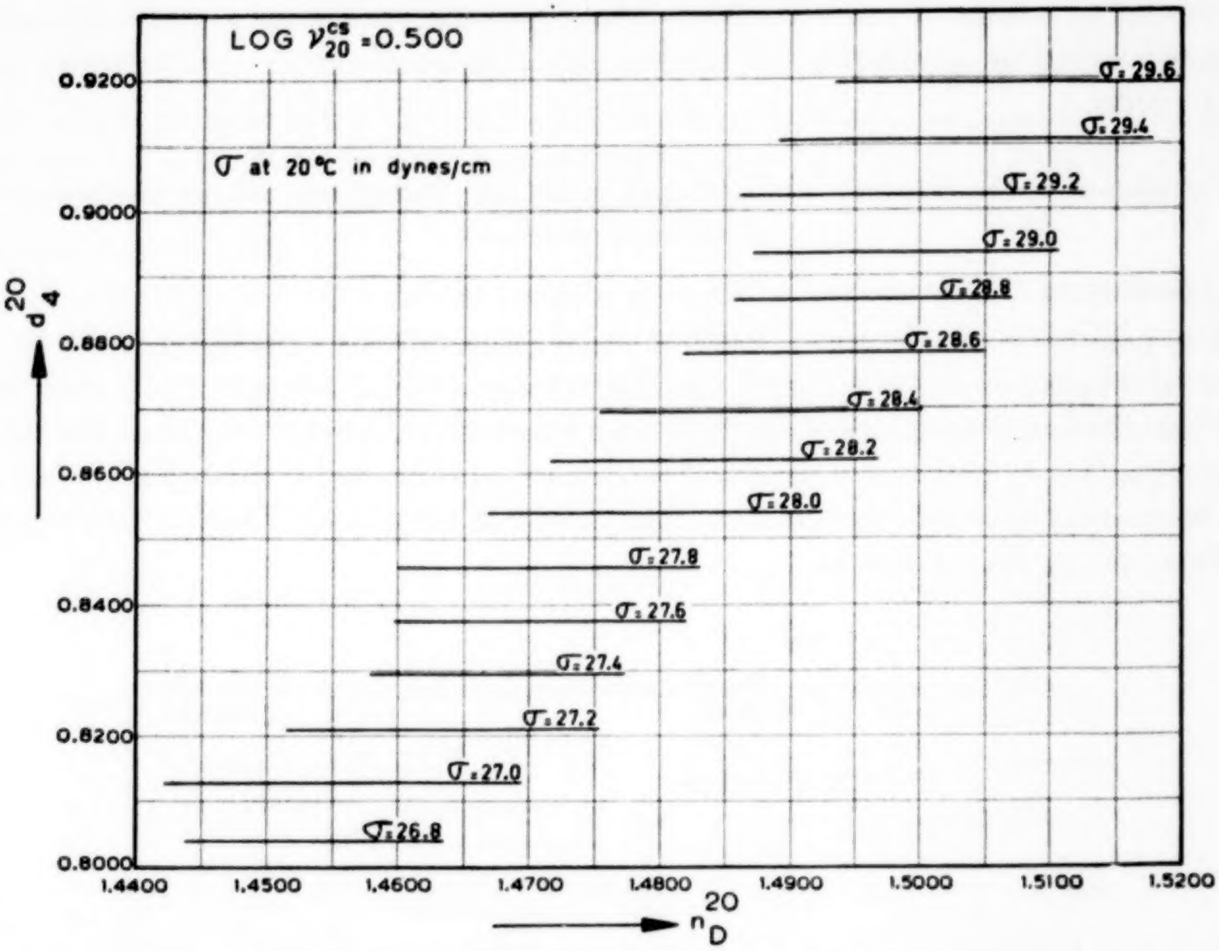

Fig. 39. Cross-section of the log $\nu-n-d$ space model at log $\nu_{20}^{cs} = 0.500$, for the determination of σ_{20}

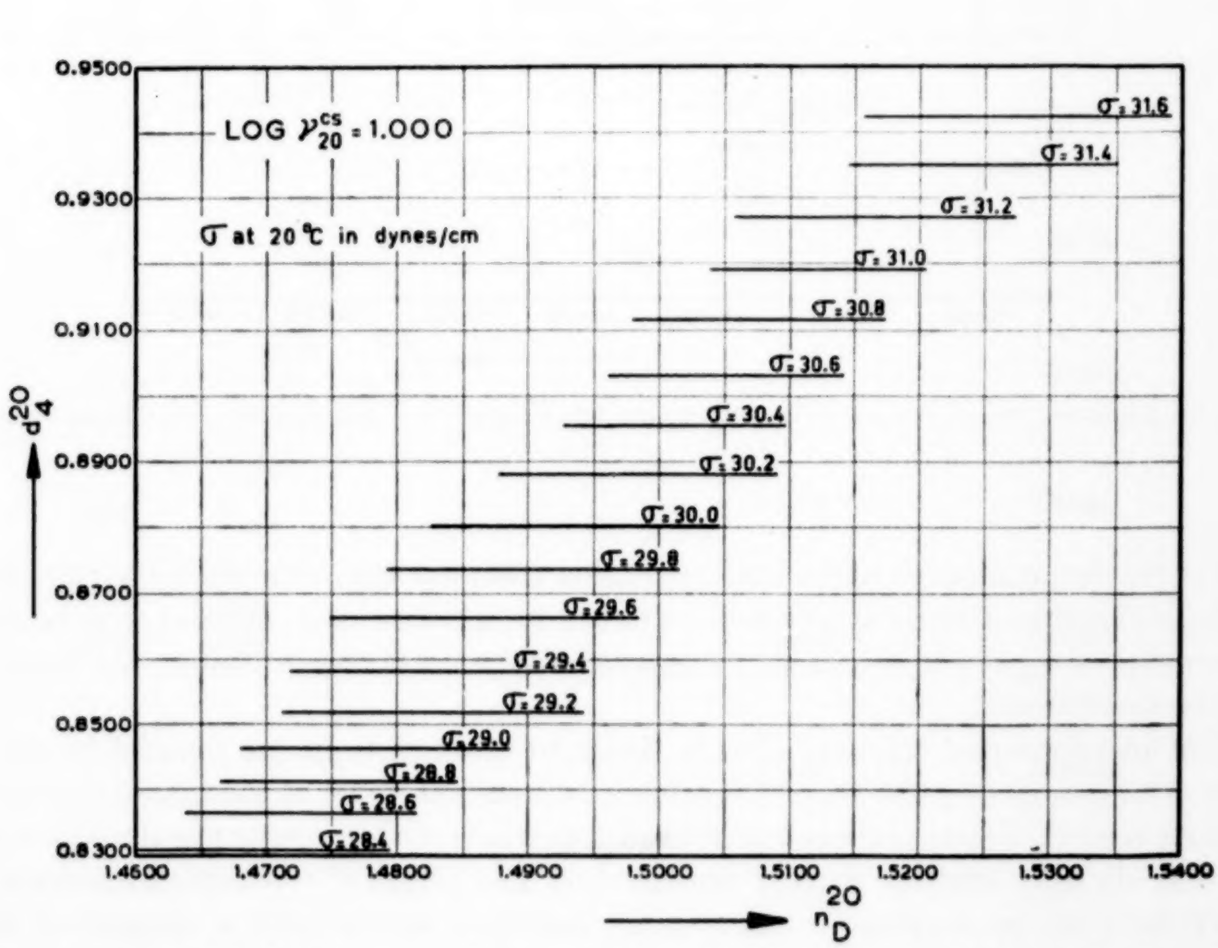

Fig. 40. Cross-section of the log $\nu-n-d$ space mode! at log $\nu_{20}^{cs} = 1.000$, for the determination of σ_{20}.

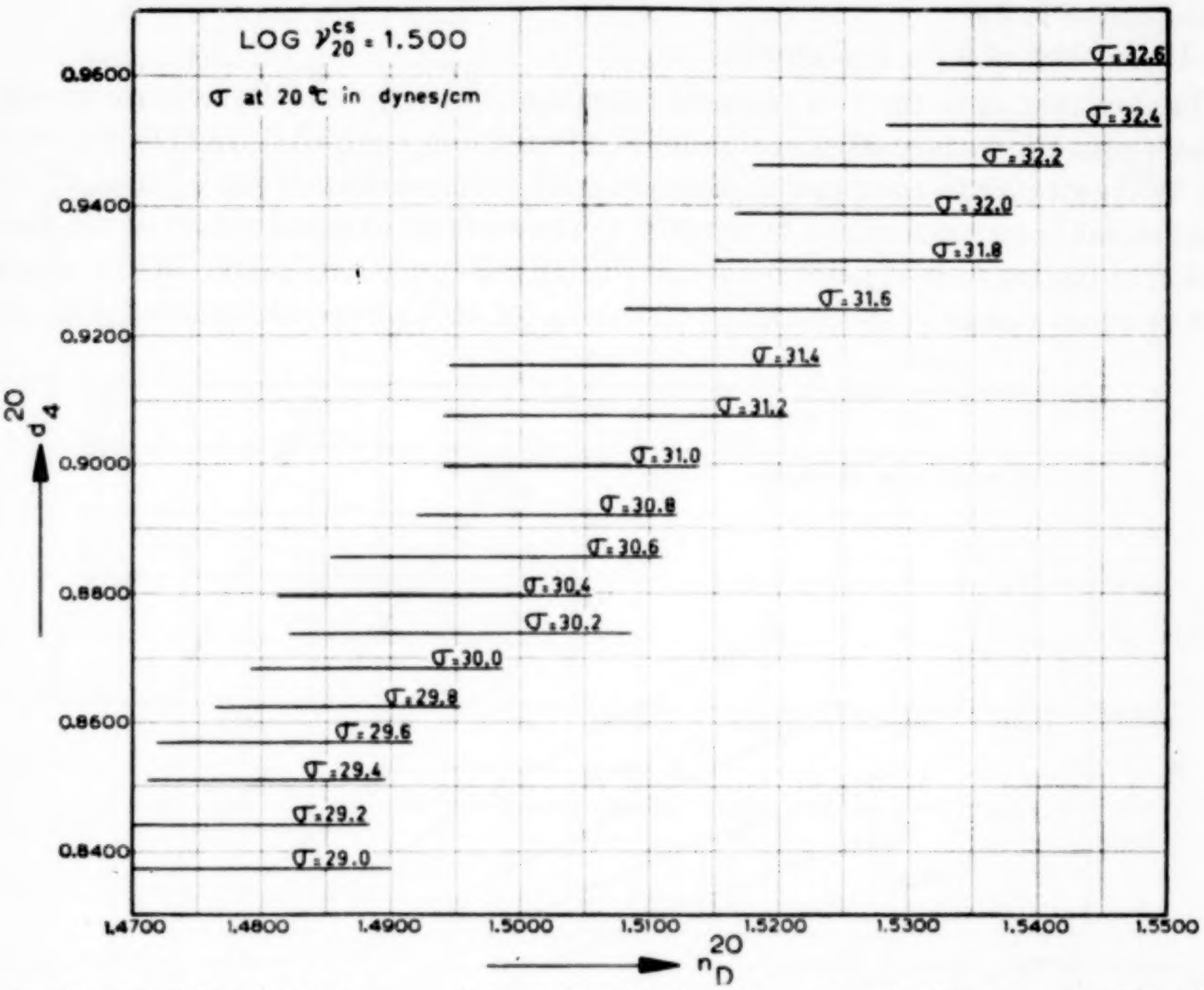

Fig. 41. Cross-section of the log $\nu - n - d$ space model at log $\nu_{20}^{cs} = 1.500$, for the determination of σ_{20}.

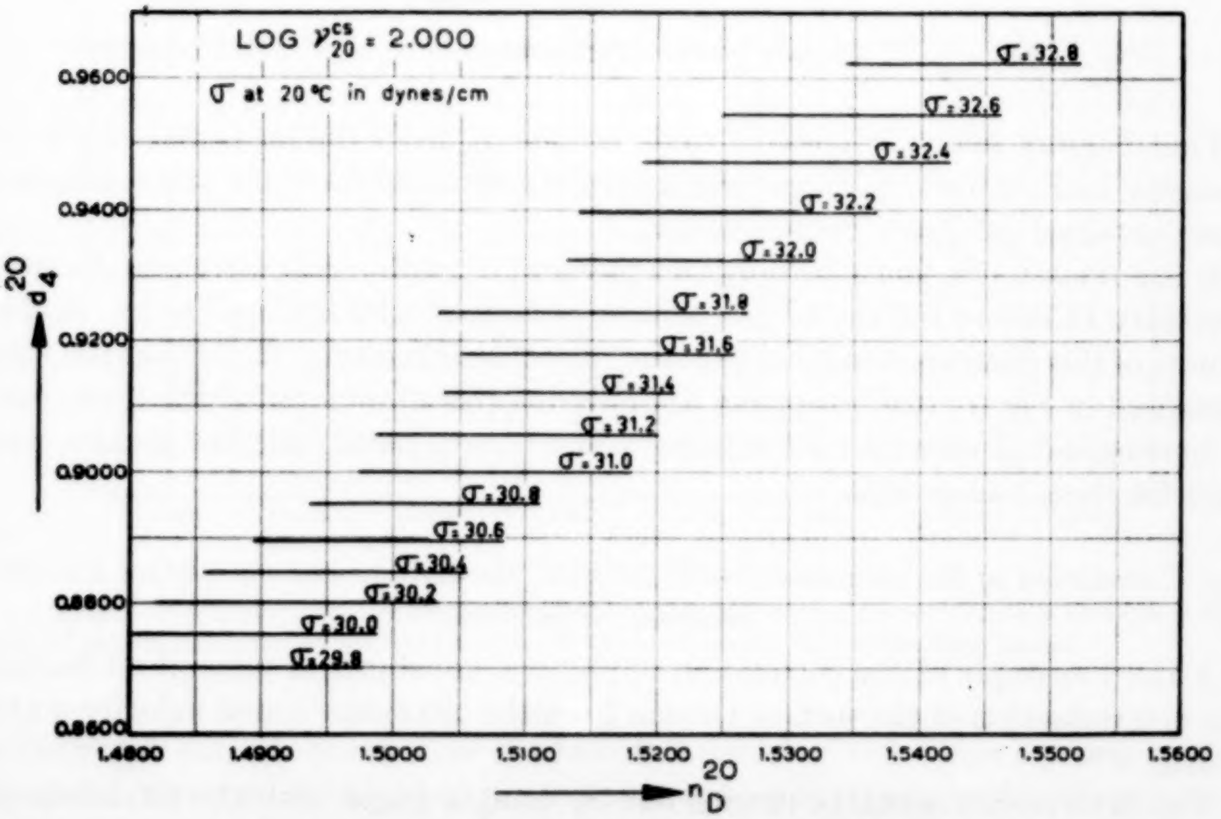

Fig. 42. Cross-section of the log $\nu - n - d$ space model at log $\nu_{20}^{cs} = 2.000$, for the determination of σ_{20}.

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(ii) *Application of a log ν-d graph*

The fact that only the two physical constants, viscosity and density, are necessary to determine the surface tension of mineral oil fractions, enabled CORNELISSEN, HARVA AND WATERMAN[21] to construct a diagram with the coordinates log ν_{20}^{cs} and d_4^{20}. This diagram has been constructed by projecting the surfaces of equal values of the surface tension in the log ν-n-d space model on the log ν-d coordinate plane. In the diagram lines of equal values of the surface tension σ_{20} (at 20°C) were constructed (Fig. 43).

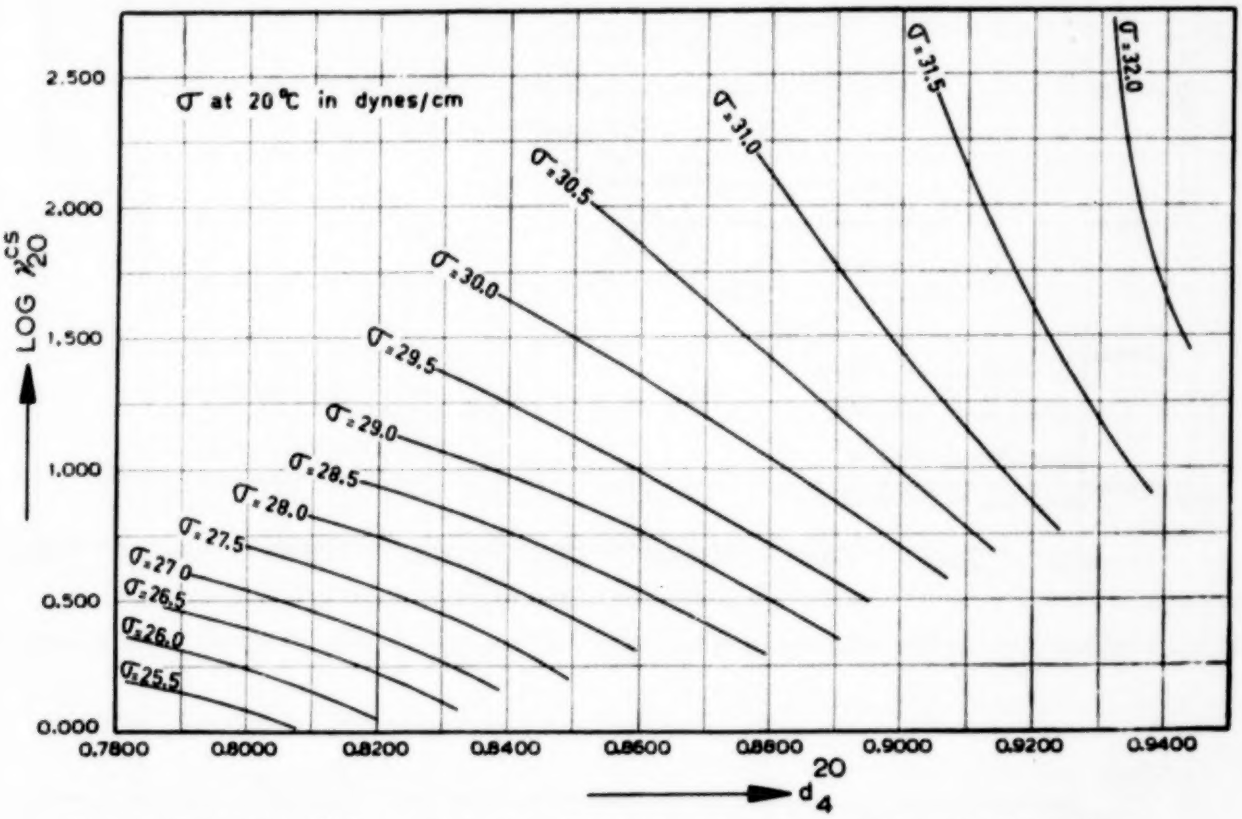

Fig. 43. Log ν_{20}^{cs}–d_4^{20} diagram for the determination of σ_{20} of mineral oil fractions.

This diagram makes it possible to determine σ_{20} from the measured values of the viscosity and the density. In general the results obtained have the same accuracy as those obtained by direct measurements.

It is a remarkable fact that only two physical constants (viscosity and density) are necessary to determine the surface tension of mineral oil fractions. The physical background of this phenomenon is not yet clear. Another remarkable fact is that the diagram presented in Fig. 43 can be applied not only to original mineral oil fractions, but also to hydrogenated mineral oil fractions, whereas in general different graphs must be used for these two groups.

c. *Correlation of the ultrasonic sound velocity, the density and the surface tension of mineral oil fractions*

A third example of the correlation of physical constants of mineral oil fractions is the determination of the surface tension from the ultrasonic sound velocity u and the density d[22].

This determination can be carried out by using a graph with the ultrasonic sound velocity u and the density d as coordinates, as shown in Fig. 44.

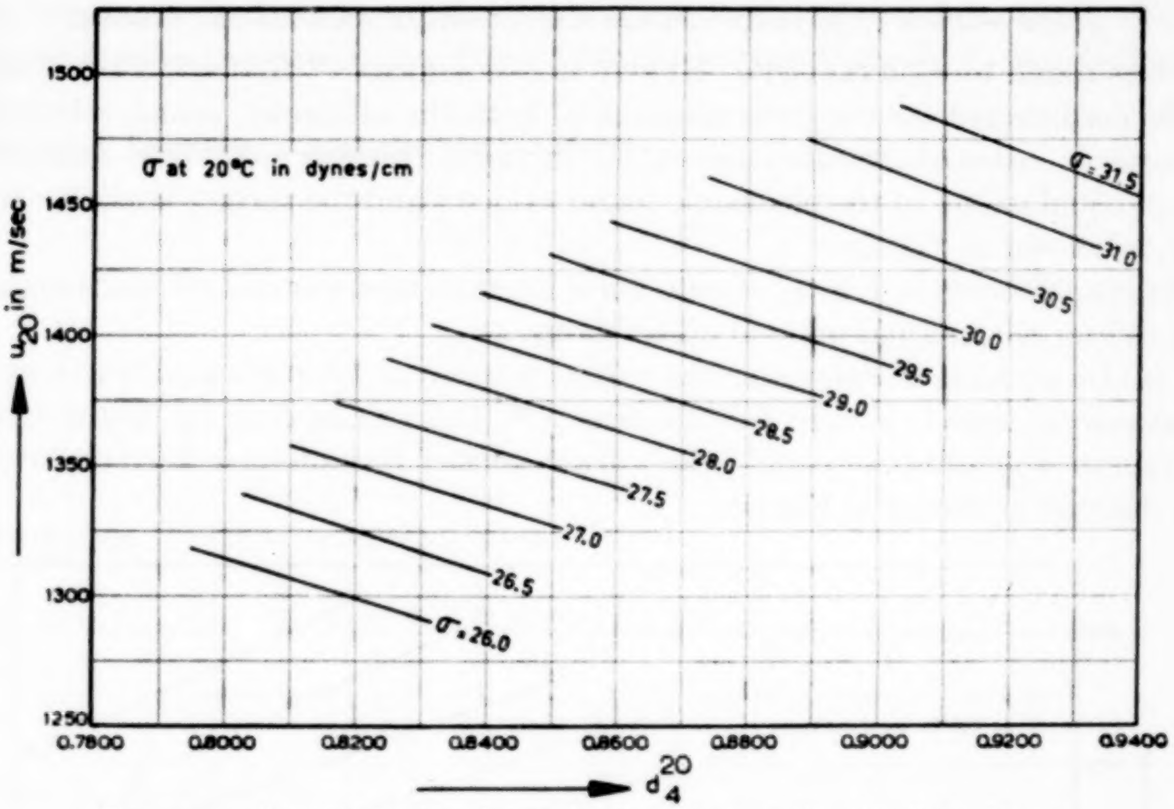

Fig. 44. *u–d* graph for the determination of σ of mineral oil fractions.

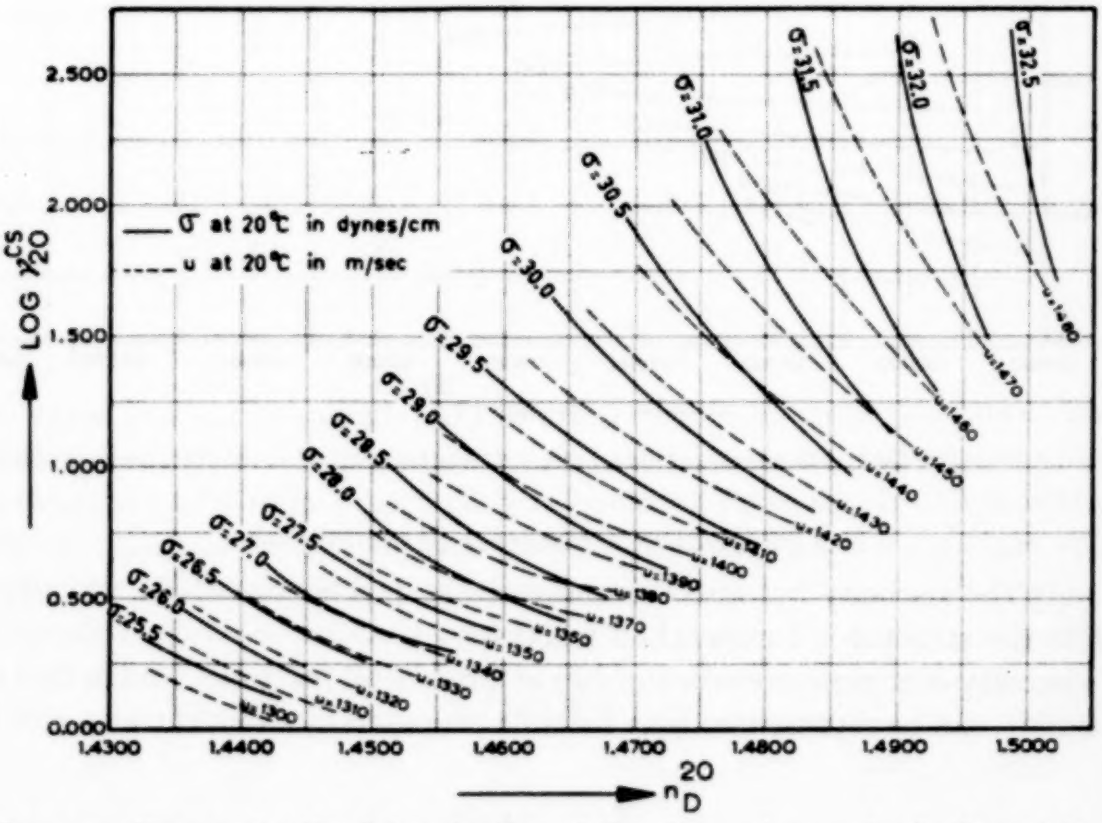

Fig. 45. Log *ν–n* diagram for the determination of the ultrasonic sound velocity and the surface tension of saturated mineral oil fractions from their viscosity and refractive index.

In the graph lines of equal values of *u* have been constructed. These lines are straight and parallel. Stress ~~must~~ be laid on the fact that the graph is only applicable to original mineral oil fractions and not to saturated mineral oil fractions.

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d. Correlation of physical constants of saturated mineral oil fractions

It was found by CORNELISSEN, HARVA AND WATERMAN[23] that a log *ν–n* diagram can be constructed for the determination of both the ultrasonic sound velocity and the surface tension of saturated mineral oil fractions. This was possible by constructing lines of equal values of the ultrasonic sound velocity and the surface tension, respectively, as shown in Fig. 45.

The graph shown in Fig. 45 is only valid for saturated mineral oil fractions and is *not* valid for the original mineral oil fractions.

It is also possible to determine the surface tension of hydrogenated fractions from the ultrasonic sound velocity and the density[22]. This can be done by means of a *u–d* diagram in which lines of equal values of the surface tension have been constructed. This diagram is shown in Fig. 46.

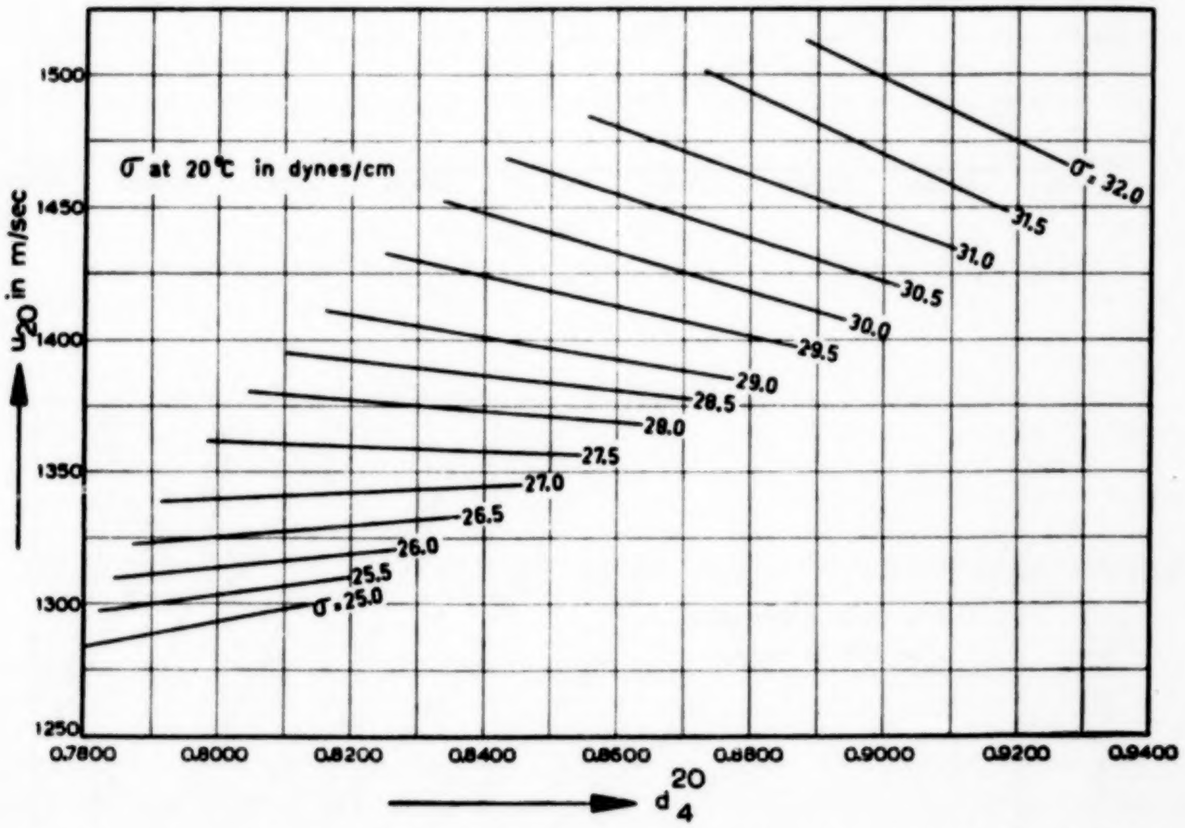

Fig. 46. *u–d* diagram for the determination of the surface tension of saturated mineral oil fractions.

e. Temperature dependence of the viscosity

Not only the viscosity but also the temperature dependence of the viscosity can be related to the structure of mineral oil fractions.

The viscosity-temperature relationship of mineral oil fractions, and in fact of many other liquids, can be represented by a formula proposed by CORNELISSEN AND WATERMAN[24]

$$\boxed{\log \nu = \frac{A}{T^x} + B} \quad \ldots\ldots\ldots\ldots \quad (45)$$

where ν denotes the kinematic viscosity in centistokes (stokes = g·cm^{-1}·sec^{-1}) and T denotes the absolute temperature in °K; A, B and x are constants. The formula has been experimentally tested over the temperature range from 10–100°C and in some cases over wider ranges.

The constants A, B and x in the formula can be calculated from three viscosity values v_1, v_2 and v_3, determined at three different temperatures T_1, T_2 and T_3, respectively.

The three following equations are obtained:

$$\log v_1 = \frac{A}{T_1{}^x} + B \quad \text{(a)}$$

$$\log v_2 = \frac{A}{T_2{}^x} + B \quad \text{(b)}$$

$$\log v_3 = \frac{A}{T_3{}^x} + B \quad \text{(c)}$$

Subtracting (b) from (a) and (c) gives:

$$\log v_1 - \log v_2 = A\left(\frac{1}{T_1{}^x} - \frac{1}{T_2{}^x}\right) \quad \text{(d)}$$

$$\log v_2 - \log v_3 = A\left(\frac{1}{T_2{}^x} - \frac{1}{T_3{}^x}\right) \quad \text{(e)}$$

Dividing (d) by (e) gives:

$$\frac{\log v_1 - \log v_2}{\log v_2 - \log v_3} = \frac{\dfrac{1}{T_1{}^x} - \dfrac{1}{T_2{}^x}}{\dfrac{1}{T_2{}^x} - \dfrac{1}{T_3{}^x}} \quad \text{(46)}$$

$$\text{If } Q = \frac{\log v_1 - \log v_2}{\log v_2 - \log v_3} \quad \text{(46a)}$$

$$\text{nd } Q = \frac{\dfrac{1}{T_1{}^x} - \dfrac{1}{T_2{}^x}}{\dfrac{1}{T_2{}^x} - \dfrac{1}{T_3{}^x}} \quad \text{(46b)}$$

then the value of x can be calculated from that of Q using equation (46b). The value of Q is calculated by means of equation (46a) from the measured viscosity values.

The calculation of x from Q according to equation (46b) can be made with the aid of a table or a diagram if for the three temperatures T_1, T_2 and T_3, certain values are used, *e.g.* 20°C, 40°C and 70°C.

An example is given in Table II and Fig. 47.

TABLE II

$Q\left\{\begin{matrix}20\\40\\70\end{matrix}\right.$	x
0.78	1
0.84	2
0.91	3
0.99	4
1.07	5

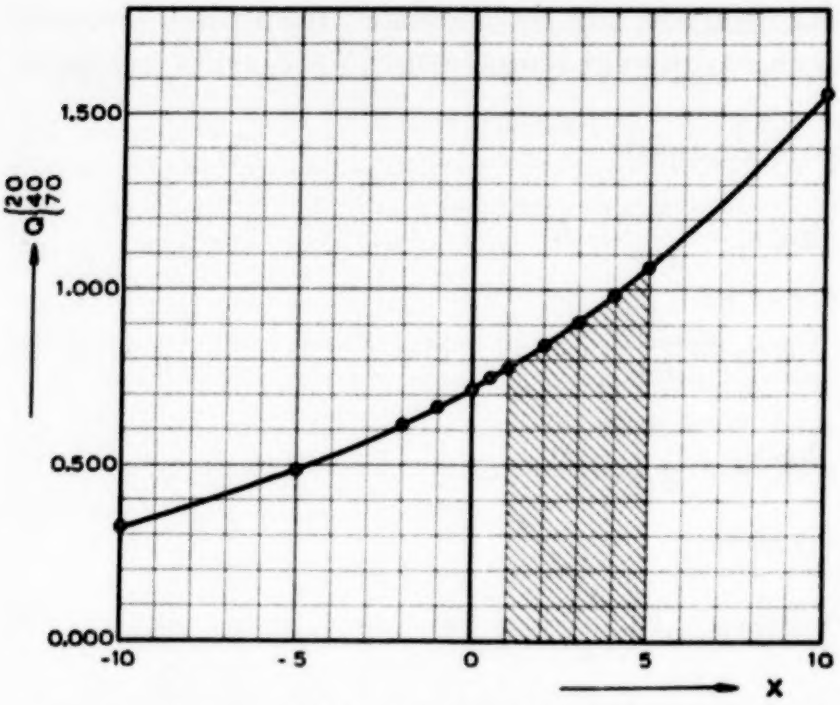

Fig. 47. Q–x diagram for the determination of the value of x from the equation $\log \nu = \frac{A}{T^x} + B$, if the value of Q from equation (46a) is known.

A more detailed table than Table II has been published[25].

x can also be calculated[25a] by means of the equation

$$x = \frac{2(\log Q - \log Q_\circ)}{\log T_3 - \log T_1}$$

in which

$$Q_\circ = \frac{\log T_1 - \log T_2}{\log T_2 - \log T_3}$$

$$Q_\circ = \lim_{x=0} Q$$

Once the value of x is known the value of A can be determined by means of the equation that can be derived from equations (a) and (c) by subtraction

$$\log \nu_1 - \log \nu_3 = A\left(\frac{1}{T_1{}^x} - \frac{1}{T_3{}^x}\right)$$

or

$$A = \frac{\log \nu_1 - \log \nu_3}{\dfrac{1}{T_1{}^x} - \dfrac{1}{T_3{}^x}} \quad \ldots\ldots\ldots\ldots \quad (47)$$

In many cases it is permissible to vary the experimental value of x about 0.5 unit, if the temperature range from 20°C to 100°C is being used, without unduly affecting the accuracy of the results of a calculation. Thus for a series of, for instance, lubricating oils with a value of x ranging from 3.0 to 4.0, the average group value of $x = 3.5$ can be chosen. In that case x may be considered as a constant for that group of oils, so that equation (47) can be altered to:

$$A = \frac{\log \nu_1 - \log \nu_3}{\text{constant}} \quad \ldots\ldots\ldots\ldots \quad (48)$$

Thus, the temperature dependence of the viscosity of these lubricating oils, being equal to A, is determined by $(\log \nu_1 - \log \nu_3)$ if the value of x is the same. If 20°C and 70°C are chosen for T_1 and T_3 this expression becomes $\log \nu_{20} - \log \nu_{70} = \log \frac{\nu_{20}}{\nu_{70}}$ (see also Fig. 48).

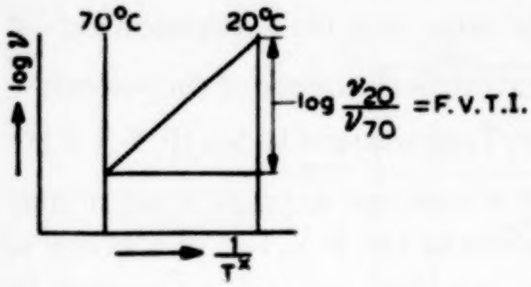

Fig. 48. Schematical representation of the viscosity-temperature relationship of liquids with a certain constant average value of x; the slope A of the line is equal to $\frac{\log(\nu_{20}/\nu_{70})}{\text{constant}}$; therefore, for this group of oils with constant x value, $\log\frac{\nu_{20}}{\nu_{70}}$ is a measure for the temperature dependence of the viscosity.

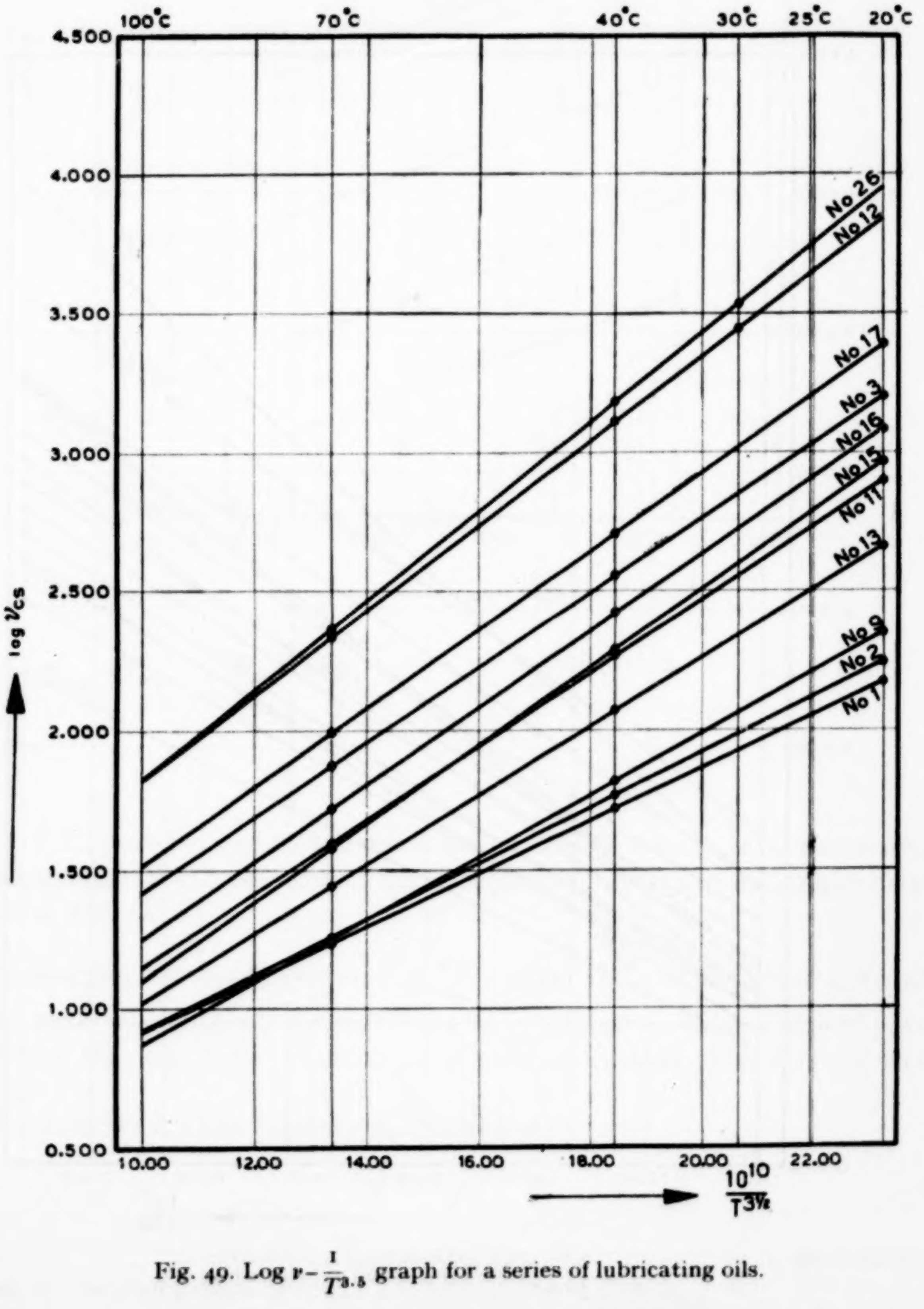

Fig. 49. Log $\nu - \frac{1}{T^{3.5}}$ graph for a series of lubricating oils.

In a particular group of oils with constant average value of x, the expression $\log \frac{\nu_{20}}{\nu_{70}}$ can be considered as an absolute index for the temperature dependence of the viscosity; $\log \frac{\nu_{20}}{\nu_{70}}$ has been given the name Fundamental Viscosity Temperature Index (F.V.T.I.)[26].

Only in the case of oils belonging to a group with a constant average x value may the values of the F.V.T.I. be compared. *E.g.* the values of the F.V.T.I. of a group of lubricating oils with an average group value of $x = 3.5$ (Figs. 49 and 50), cannot be compared with the values of the F.V.T.I. of a group of silicone oils with an average group value of $x = 1.0$ (Fig. 51).

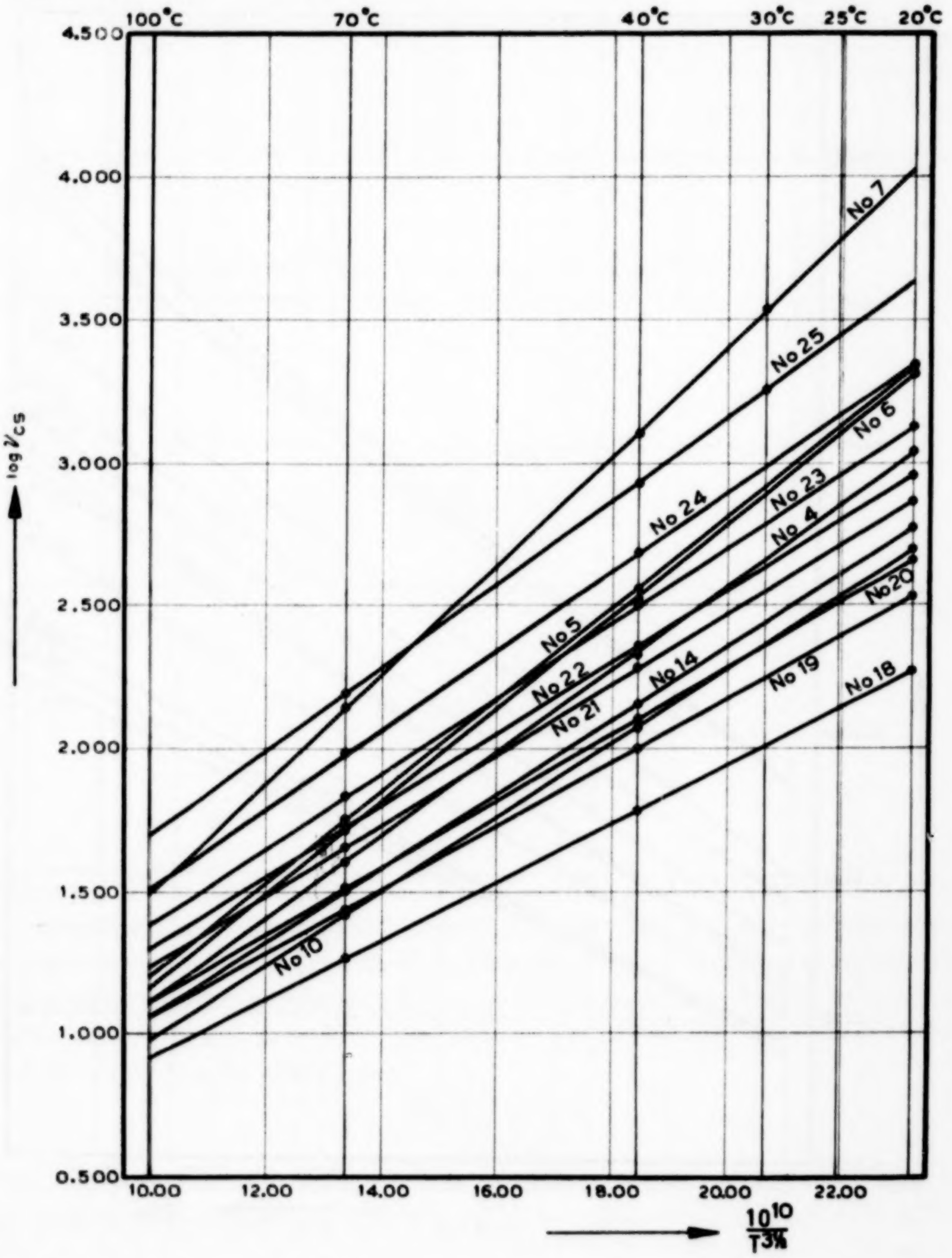

Fig. 50. Log $\nu - \frac{1}{T^{3.5}}$ graph for a series of lubricating oils.

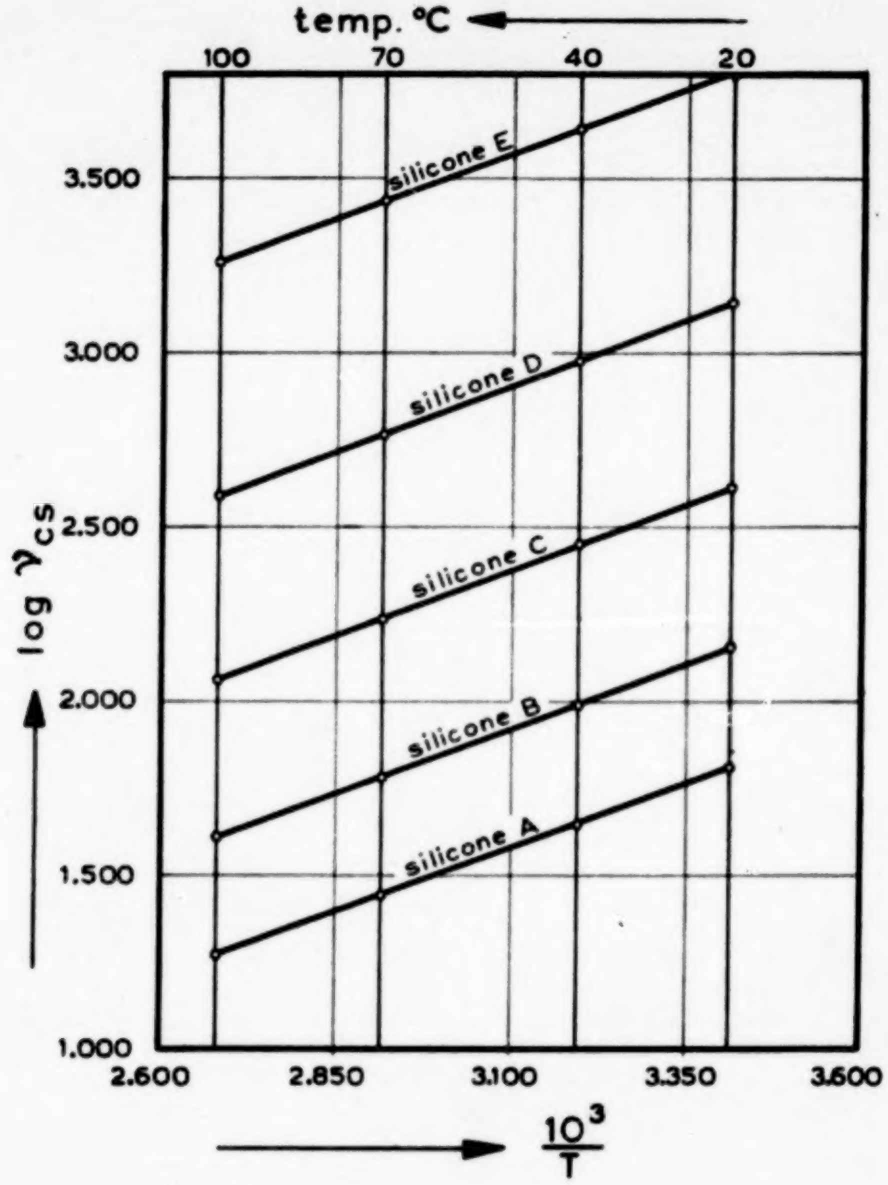

Fig. 51. Log $\nu - \frac{1}{T}$ for a series of silicone oils.

The F.V.T.I. can be used to determine the number of rings in saturated fractions. CORNELISSEN AND WATERMAN constructed a diagram for this purpose[27], which diagram is shown in Fig. 52.

In the diagram the coordinates are log $\frac{\nu_{20}}{\nu_{70}}$ and the refractive index at 20°C, n_D^{20}.

In the same way an x-n_D^{20} diagram[25] can be constructed, which makes it possible to determine the ring content of saturated mineral oil fractions. This diagram is given in Fig. 53.

In this diagram x is the exponent in the formula

$$\log \nu = \frac{A}{T^x} + B \qquad \text{. . . . . (45)}$$

This method has been applied by GEERARDS AND WATERMAN[28] to hydrocarbon oils obtained by hydrogenation of coal.

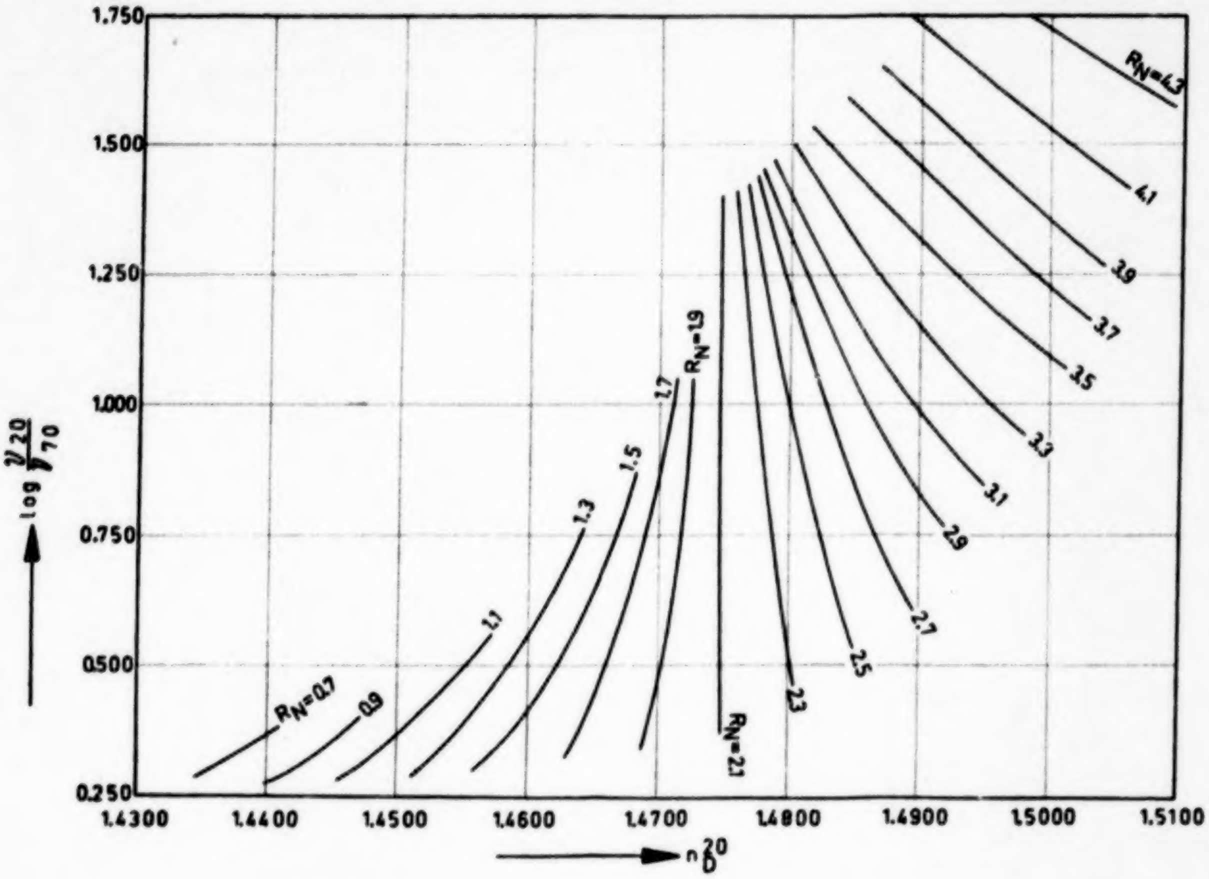

Fig. 52. Log $\frac{\nu_{20}}{\nu_{70}} - n_D^{20}$ diagram for the determination of the number of rings in saturated mineral oil fractions.

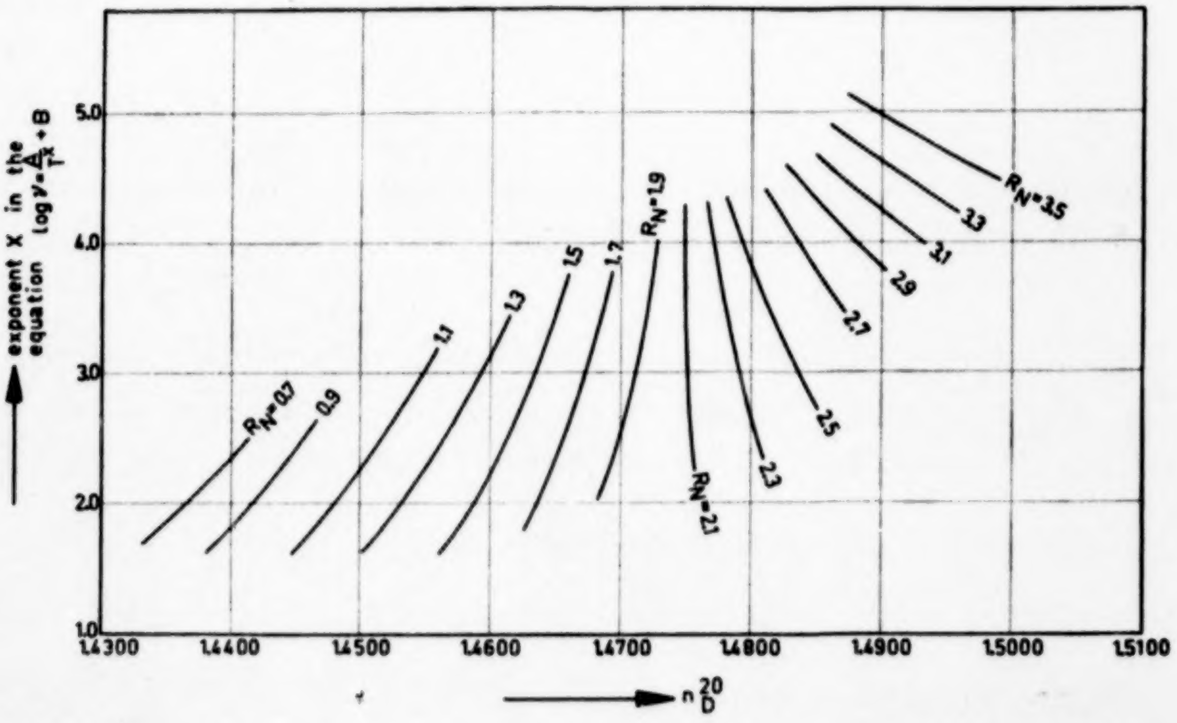

Fig. 53. $x - n_D^{20}$ diagram for the determination of the ring content of saturated mineral oil fractions.

4. ANALYSIS OF BRANCHED HYDROCARBON MIXTURES

a. Introduction

When determining the degree of branching of hydrocarbon mixtures by means of physical constants, especially those physical constants or functions thereof should be chosen that show the necessary sensitivity to the presence of branchings. Particularly the parachor and the magneto-optical rotation have found application.

There are mainly two problems that hamper the development of reliable methods for the analysis of branched hydrocarbon mixtures.

In the first place an unambiguous definition of the "degree of ramification" is very difficult, especially for naphthenic hydrocarbons, which are generally present in hydrocarbon mixtures. DE BOOIJS[29] gave the following definition:

φ = *the number of n-alkyl groups building up the hydrocarbon molecule, minus one*

thus trying to combine both paraffinic and naphthenic hydrocarbons in the same system. This, however, results in negative values of φ for cyclohexane, decalin, etc., and it is quite doubtful whether such hydrocarbons conform to a general system based on this relatively arbitrary definition of the degree of branching φ. WESTERDIJK *et al.*[30,10a] defined the degree of branching N_v in saturated individual molecules as:

$$N_v = \frac{N_{\mathrm{CH_3}} - 2 + 3\,R_T}{N_c} \quad \ldots\ldots\ldots\ldots (49)$$

where $N_{\mathrm{CH_3}}$ = the number of methyl groups in the molecule
R_T = the number of naphthenic rings per molecule
N_c = the number of carbon atoms per molecule
N_v is related to one carbon atom.

The naphthenic ring is thus considered as a form of branching that contributes three times as much as a side chain.

Secondly there is no direct method for determining the degree of branching (φ or N_v) of mineral oil fractions or similar hydrocarbon mixtures. Direct correlation of φ or N_v with any particular physical constant is therefore impossible. The existing methods have all been based on correlating the data obtained from a limited number of individual hydrocarbons with their degree of branching, and consequently have a more or less limited and approximate character when applied to mineral oil fractions and other hydrocarbon mixtures. It should therefore be emphasized that the various methods of branching analysis are only qualitative, or at best semi-quantitative. For comparative studies they may be of some value, but quantitative data generally cannot be obtained.

b. The Faraday effect

The phenomenon of the rotation of the plane of polarization of light by substances when placed in a magnetic field is called the Faraday effect. The angle of rotation (α) depends on the nature of the substance:

$$\alpha = V\,H\,L\cos\beta$$

V is called the Verdet-constant; it depends only slightly on the temperature, but varies markedly with the wavelength of the light; measurements are normally carried out with a sodium-lamp (Na-D line) at 20°C; V is generally given as $\frac{100\ \mathrm{min}}{\mathrm{cm\cdot gauss}}$ and indicated in this case by $100\ V_D^{20}$.

H is the strength of the magnetic field in gauss, L is the length of the path travelled by the light through the substance, β is the angle between the beam of light and the magnetic field lines.

Absolute determinations of V are extremely difficult. For routine measurements relative methods have been worked out[29,31], in which the experimental material is compared directly with a standard liquid (*e.g.* water); these methods also require a relatively complicated apparatus and skilled operators to obtain a reasonable accuracy ($\pm 0.05\%$).

WESTERDIJK *et al.*[30] have shown that the Verdet constant of saturated hydrocarbons is not so much related to the degree of branching φ as to the degree of branching defined by N_v. DE BOOIJS[29] succeeded in correlating N_v and V for a large number of paraffinic and naphthenic hydrocarbons:

$$N_v = \frac{(N_{CH_3} - 2) + 3R_T}{N_c} = \frac{100\,V - 1.456 + \dfrac{1.56}{N_c}}{0.200} \quad \ldots\ldots (50)$$

thus indicating a method of estimating N_{CH_3}, the number of methyl groups of the individual saturated hydrocarbons, when V, N_c and R_T are known (*cf.* Fig. 54).

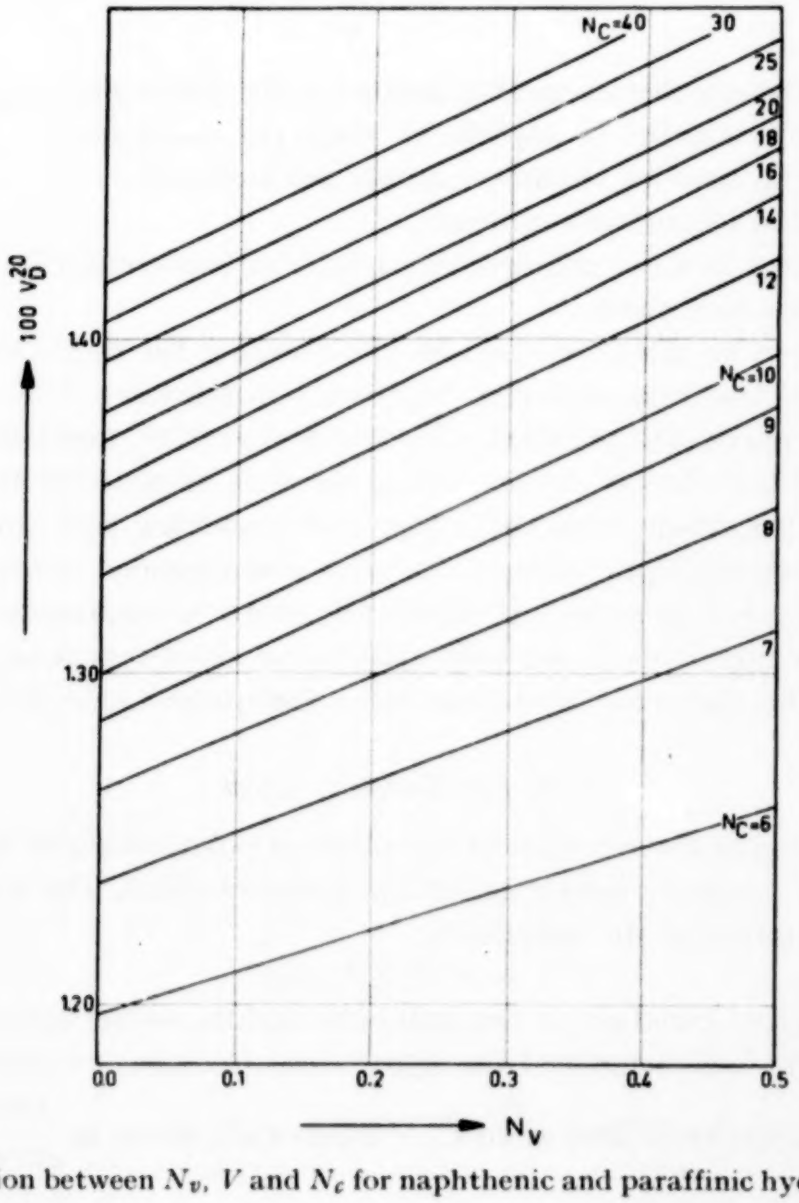

Fig. 54. Relation between N_v, V and N_c for naphthenic and paraffinic hydrocarbons.

The method can also be applied to aromatic- and olefin-free hydrocarbon mixtures (*cf.* Table III); in these cases N_c can be calculated from the average molecular weight M by means of the formula

$$N_c = \frac{M + 2\,R_T - 2}{14.026} \quad \ldots\ldots\ldots\ldots\ldots \quad (51)$$

c. The magneto-optical rotation[31]

The molecular magneto-optical rotation D is a function of the refractive index n, the density d, the Verdet constant V and the molecular weight M:

$$D = \frac{9\,n\,V\,M}{(n^2 + 2)^2 d} \quad \ldots\ldots\ldots\ldots\ldots \quad (52)$$

This function shows a certain resemblance to that of the molecular refraction $r_{\mathrm{mol.}}$:

$$r_{\mathrm{mol.}} = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} \quad \ldots\ldots\ldots\ldots\ldots \quad (53)$$

However, in the analysis of saturated hydrocarbon mixtures, D has proved to be not only highly sensitive to the presence of rings (like $r_{\mathrm{mol.}}$), but also to ramifications in the molecules. When comparing D and $r_{\mathrm{mol.}}$ of paraffinic or naphthenic hydrocarbons with those of corresponding *n*-alkanes of equal molecular weight ($D_{n\text{-alkane}}$ and $r_{\mathrm{mol.}(n\text{-alkane})}$, respectively), it can be stated that

$$\varphi = a(D - D_{n\text{-alkane}}) - b(r_{\mathrm{mol.}} - r_{\mathrm{mol.}(n\text{-alkane})}) \quad \ldots\ldots \quad (54)$$

where: $D_{n\text{-alkane}} = 0.01309M + 0.1544$

$r_{\mathrm{mol.}(n\text{-alkane})} = 0.3309M + 1.424$

M = the molecular weight.

a and b are constants depending on the nature of the homologous hydrocarbon series considered. In this equation φ is expressed in terms of $(D - D_{n\text{-alkane}})$ and $(r_{\mathrm{mol.}} - r_{\mathrm{mol.}(n\text{-alkane})})$; the form of the equation follows from the consideration that for saturated hydrocarbons these two expressions are functions of both ring content and degree of branching; the dependency of $(r_{\mathrm{mol.}} - r_{\mathrm{mol.}(n\text{-alkane})})$ on φ is, however, small in comparison with that of $(D - D_{n\text{-alkane}})$.

For *paraffinic hydrocarbons* the following expression is a good approximation:

$$\varphi = 26.8\,(D - D_{n\text{-alkane}}) - 6.71\,(r_{\mathrm{mol.}} - r_{\mathrm{mol.}(n\text{-alkane})}) \quad \ldots\ldots \quad (55)$$

For *saturated mineral oil fractions* the following formula can be deduced:

$$\varphi = 30.7\,(D - D_{n\text{-alkane}}) - 3.08\,(r_{\mathrm{mol.}} - r_{\mathrm{mol.}(n\text{-alkane})}) \quad \ldots\ldots \quad (56)$$

The method has been applied to saturated aromatic and olefin-free mineral oil fractions and hydrogenated polymers (*cf.* Table III and IV).

DE BOOIJS[29] considered the degree of branching φ also in terms of the *apparent ring-numbers* $R_T^{r_{\mathrm{mol.}}}$ and R_T^D, which, for distinct groups of non-branched hydrocarbons are equal to the real ring-number R_T ($R_T = R_T^{r_{\mathrm{mol.}}} = R_T^D$), but differ from it when branchings are present. According to DE BOOIJS φ is given by the general equation:

TABLE III

BRANCHING ANALYSIS OF RUMANIAN FRACTIONS (TIN 5)

Fraction	n_D^{20}	d_4^{20}	$r_{spec.}^{20}$	mol. wt.	σ dyne/cm 20°C	$p = \frac{\sigma^{1/4}}{d}$	100 V_D^{20}	$r_{mol.}$	D	P	n–d–M analysis			Extended ring analysis*		Estimation of φ from			Estimation of N_{CH_3}
											R_T	R_A	%C_A	R_T	φ	M, D and $r_{mol.}$**	M, P, $r_{mol.}$ and %C_A***		from 100 V_D^{20} and N_c****
1	1.4483	0.8029	0.3336	158	26.23	2.819	—	52.71	—	445.4	0.8	0.2	11	—	—	—	0.6	0	—
1 hydrogenated	1.4354	0.7857	0.3324	164	25.83	2.870	1.367	54.51	2.236	470.7	0.7	0	0	0.7	1.5	1.6	0.8	1	2.5
2	1.4539	0.8123	0.3333	172	26.89	2.804	—	57.33	—	482.3	0.9	0.2	12	—	—	—	0.8	1	—
2 hydrogenated	1.4405	0.7963	0.3313	175	26.66	2.854	1.381	57.98	2.369	499.5	0.8	0	0	0.8	1.5	1.8	0.8	1	2.7
4	1.4662	0.8328	0.3327	208	28.37	2.772	—	69.20	—	576.6	1.0	0.4	15	—	—	—	0.9	1	—
4 hydrogenated	1.4503	0.8153	0.3298	219	27.68	2.814	1.395	72.23	2.905	616.3	1.0	0	0	0.95	3	1.6	1.5	1.5	2.0
6	1.4733	0.8469	0.3314	264	29.43	2.751	—	87.49	—	726.3	1.2	0.4	14	—	—	—	1.3	1	—
6 hydrogenated	1.4580	0.8299	0.3288	277	29.13	2.799	1.417	91.08	3.646	775.3	1.2	0	0	1.15	3.5	2.0	1.7	1.5	2.3
7	1.4795	0.8580	0.3308	291	29.94	2.734	—	96.26	—	795.6	1.4	0.5	14	—	—	—	1.8	2	—
7 hydrogenated	1.4623	0.8389	0.3279	300	29.61	2.788	1.425	98.37	3.916	836.4	1.4	0	0	1.4	3	2.1	1.7	1.5	2.3

* According to Figs. 59 and 60, eqns. (65) and (66). ** According to eqns. (54) and (56). *** According eqn. (69) and Fig. 61, respectively
**** According to Fig. 54, eqn. (50).

TABLE IV

BRANCHING ANALYSIS OF HYDROGENATED POLYMERS

Starting material	Conditions of polymerization	Physical constants of hydrogenated polymers										Estimation of R_T		Estimation of φ		Estimation of N_{CH_3}
		n_D^{20}	d_4^{20}	$r_{spec.}^{20}$	mol. wt.	σ dyne/cm	$p = \frac{\sigma^{1/4}}{d}$	100 V_D^{20}	%H (ultimate analysis)	$r_{mol.}$	D	from %H and mol. wt.	from extended ring analysis*	from extended ring analysis*	from M, D and $r_{mol.}$**	from 100 V_D^{20} and N_c***
Propylene	BF_3 at —35°C	1.4617	0.8315	0.3304	417	28.4	2.776	1.462	14.74	137.78	5.637	0.2	0.5	12.5	11.6	10.5
Propylene	BF_3 at —30°C	1.4620	0.8324	0.3303	420	28.4	2.773	1.465	14.73	138.71	5.682	0.2	0.45	13	11.7	10.5
Propylene	BF_3 at —70°C	1.4649	0.8340	0.3314	399	28.4	2.768	1.478	14.80	132.23	5.424	0.0	0.0	16	9.4	13
Isobutene	silicotungstic acid 170°C	1.4354	0.7794	0.3351	199	24.2	2.846	1.426	15.05	66.65	2.853	0.2	0.0	7	6.8	7
Isobutene	silicotungstic acid 170°C	1.4237	0.7570	0.3369	171	—	—	1.384	15.61	57.61	2.470	−0.2	—	—	4.8	6
Cyclohexene	silicotungstic acid 180°C	1.4777	0.8847	0.3198	178	31.4	2.676	1.407	13.25	56.92	2.151	2.2	2.2	1	0.2	0.5
Cyclohexene	silicotungstic acid 180°C	1.5138	0.9569	0.3145	320	—	—	1.502	12.64	100.64	3.716	4.2	—	—	1.3	0

* According to Figs. 59 and 60, eqns. (65) and (66). ** Eqns. (54) and (55) for polymers of propylene and isobutene; eqns. (54) and (56) for cyclohexene polymers. *** According to Fig. 54, eqn. (50).

$$\varphi = p(R_T - R_T^D) + q(R_T - R_T^{r_\text{mol.}}) \quad \ldots\ldots\ldots \quad (57)$$

in which p and q are constants depending on the nature of the hydrocarbons; $R_T^{r_\text{mol.}}$ and R_T^D are given by equations (60) and (61).

Equation (57) shows the relation between φ and both the molecular magneto-optical rotation D and the molecular refraction $r_\text{mol.}$, although $r_\text{mol.}$ is much less influenced by the presence of branchings:

$$R_T^{r_\text{mol.}} - R_T << R_T^D - R_T \qquad (cf.\ \text{Fig. } 55)$$

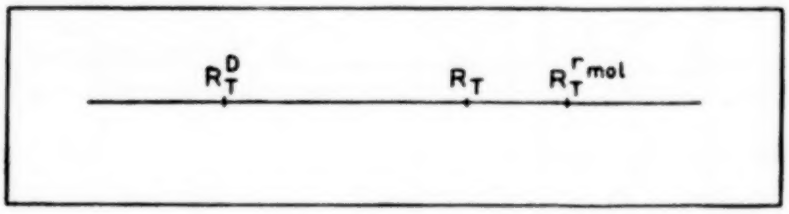

Fig. 55. Situation of the apparent ring-numbers $R_T^{r_\text{mol.}}$ and R_T^D in respect to the real ring number R_T for saturated hydrocarbons, according to DE BOOIJS[29].

For *saturated mineral oil fractions* the following holds within the limits of accuracy of determination:

$$R_T^{r_\text{mol.}} = R_T \quad \ldots\ldots\ldots\ldots\ldots \quad (58)$$

and φ is given by:

$$\varphi = 5.1\ (R_T^{r_\text{mol.}} - R_T^D) \quad \ldots\ldots\ldots\ldots \quad (59)$$

$$\text{where } R_T^{r_\text{mol.}} = \frac{0.3309M + 1.424 - r_\text{mol.}}{1.654} \quad \ldots\ldots \quad (60)$$

$$R_T^D = \frac{0.01309M + 0.1542 - D}{0.1662}. \quad \ldots\ldots\ldots \quad (61)$$

Since $R_T^{r_\text{mol.}}$ and R_T^D can be graphically represented, estimation of φ from $r_\text{mol.}$, D and M can be executed relatively easily when the proper graphs are available.

d. The parachor

(*i*) The molecular parachor P was introduced as an additive function by SUGDEN[32]:

$$P = \frac{\sigma^{\frac{1}{4}} \cdot M}{d - D_v} \quad \ldots\ldots\ldots\ldots\ldots \quad (62)$$

where σ = surface tension (dyne/cm)
d = density of the liquid
D_v = density of the vapor in equilibrium with the liquid under the conditions of measurement.

When P is determined at 20°C the value of D_v in the formula may be neglected for values of $M > 150$.

MUMFORD AND PHILLIPS[33] were the first to evaluate the influence of chain branching on the molecular parachor of hydrocarbons. They calculated values for the atomic parachors, which formed the basis for the specific parachor *vs.* molecular weight diagram of LEENDERTSE AND WATERMAN[34] (Fig. 56). In this diagram curves are drawn representing non-branched paraffins, mono-cyclic six-carbon-ring naphthenes with *one* non-branched side-chain, etc. For non-branched hydrocarbon mixtures the average number of rings estimated with this diagram is equal to the value obtained with the aid of specific refraction and molecular weight in the ring analysis diagram (*cf.* Fig. 3); when branchings are present there appears to be a difference between the two ring-numbers, which, according to LEENDERTSE AND WATERMAN, amounts to about 0.1 ring per branching.

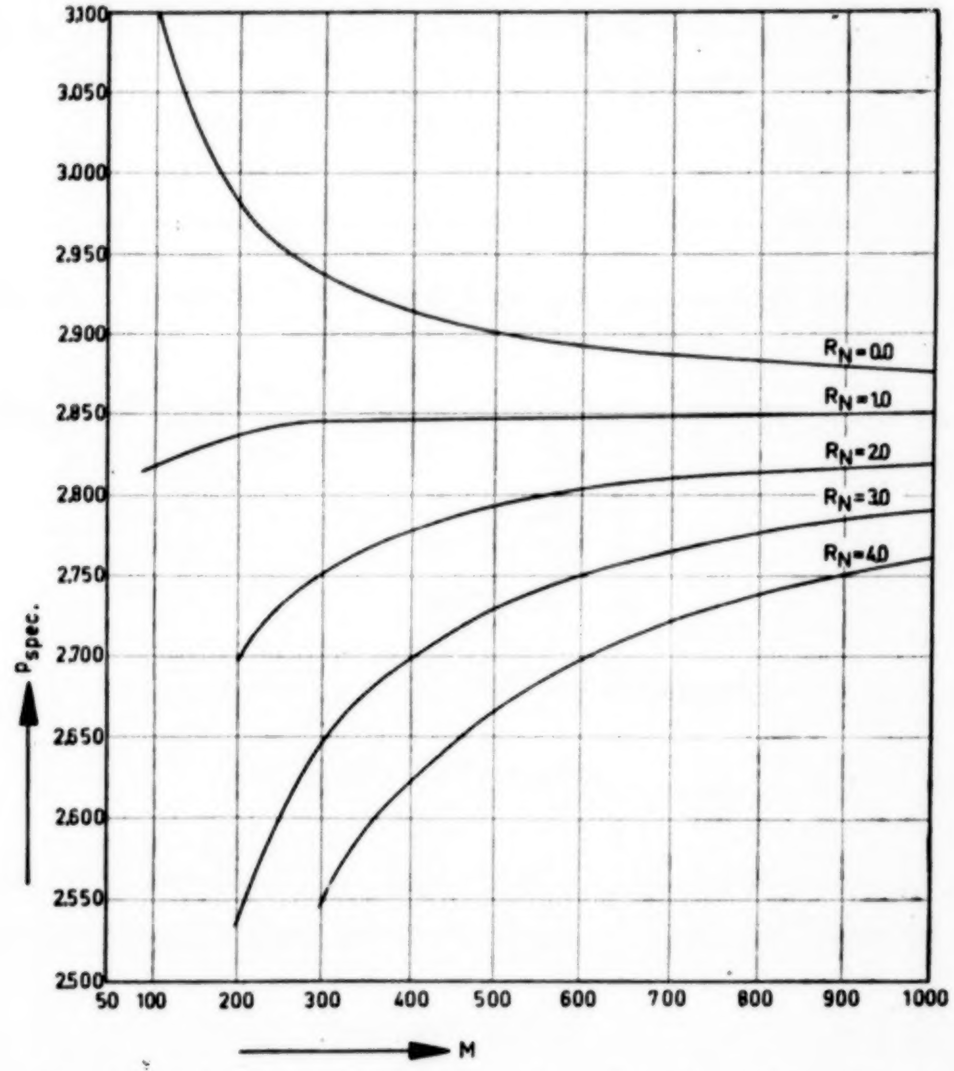

Fig. 56. Diagram for saturated non-branched hydrocarbons (based on values of the atomic parachor given by MUMFORD AND PHILLIPS) according to LEENDERTSE AND WATERMAN[34].

(*ii*) WEBER *et al.*[35], in a study on the isomerization of paraffin wax, made use of analogous diagrams, which were, however, based exclusively on reliable data of a number of *n*-alkanes and *n*-alkyl-cyclohexanes at 20° and 70°C, taken from A.P.I.-project 44[36] (*cf.* Figs. 57 and 58). They concluded that the presence of one branching in a *n*-alkane causes a ring difference $\triangle R$ of 0.09 (about 0.1) rings between the values obtained from Figs. 57 and Fig. 58, respectively:

$$\varphi = 11 \triangle R \quad \ldots\ldots\ldots\ldots\ldots (63)$$

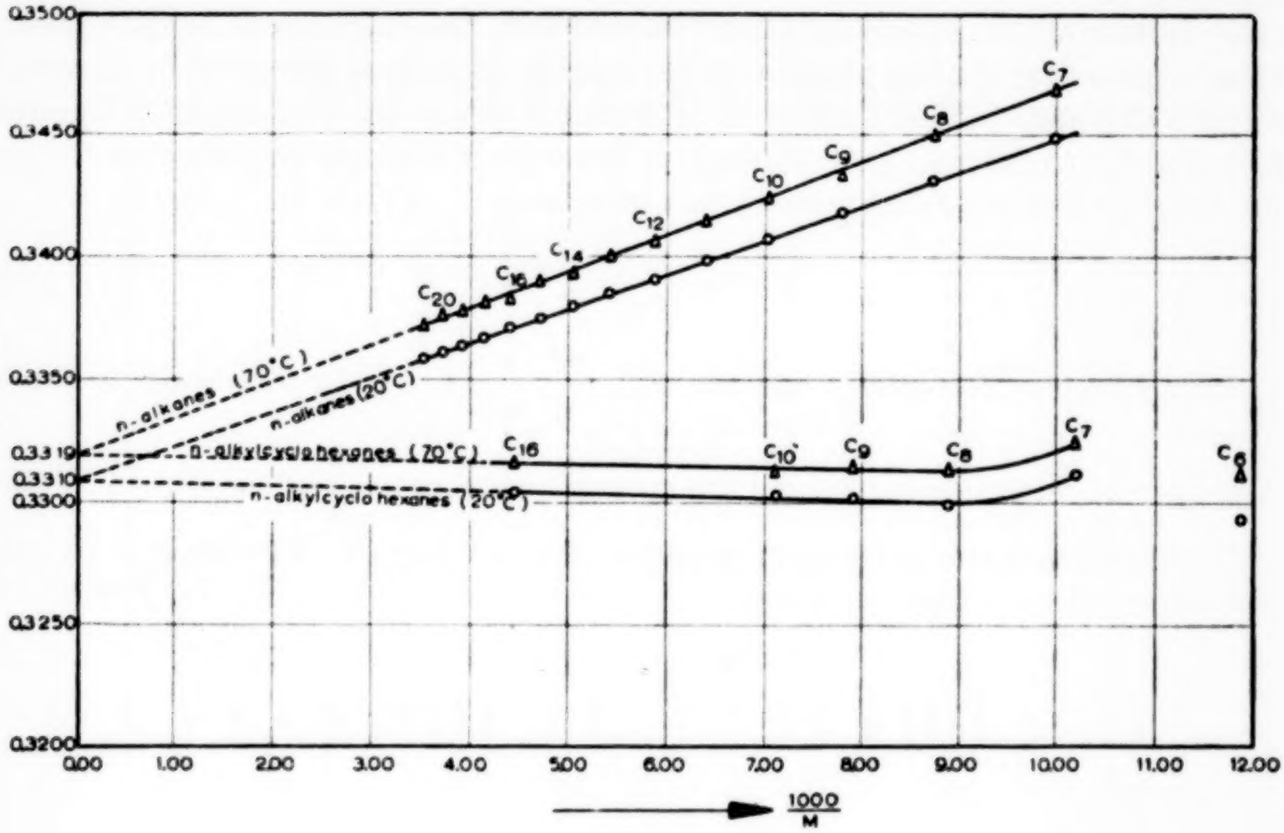

Fig. 57.

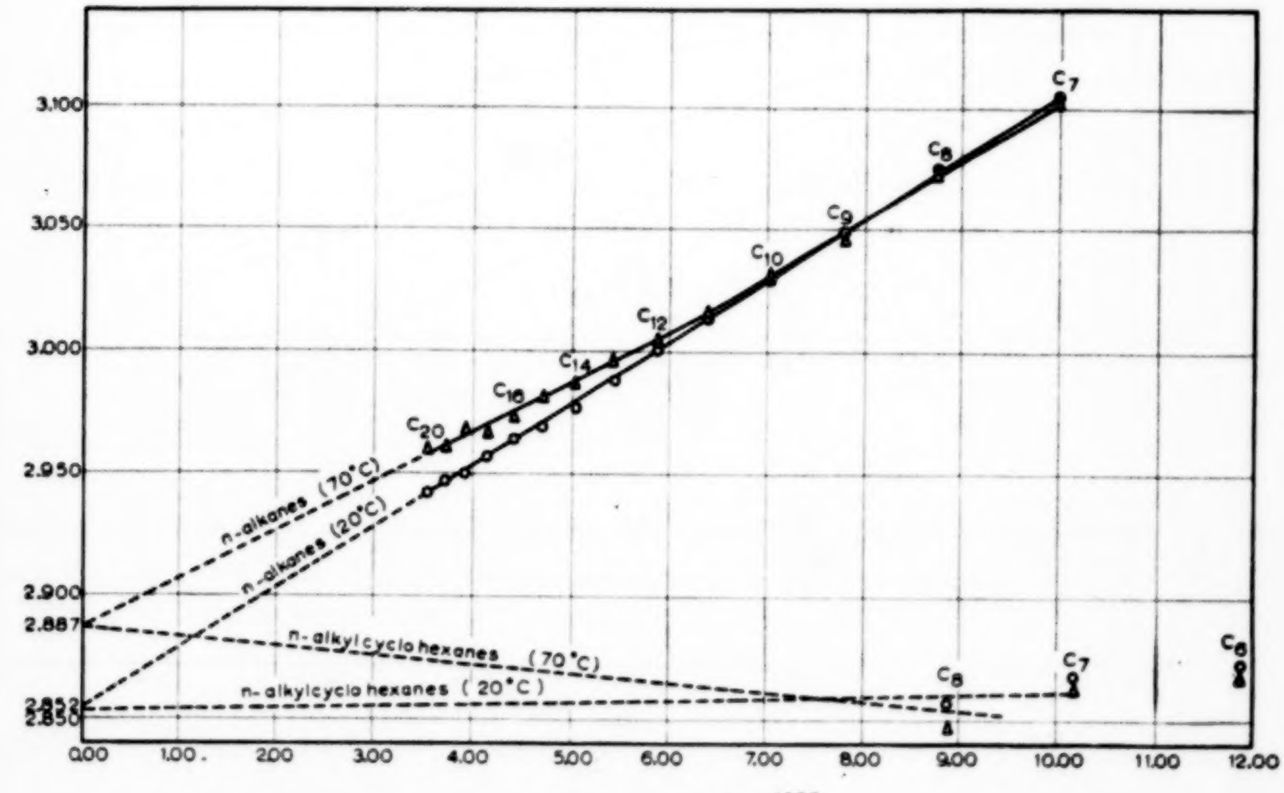

Fig. 58.

Figs. 57 and 58. Diagrams representing specific refraction *vs.* $\frac{1}{M}$ and specific parachor *vs.* $\frac{1}{M}$ based on A.P.I. data of *n*-alkanes and *n*-alkyl-cyclohexanes at 20° and 70°C[36].

(*iii*) BOELHOUWER AND WATERMAN[9] showed that the diagrams of WEBER form a valuable means for the ring analysis and branching analysis of saturated hydrocarbon mixtures of widely different degree of branching. Use was made of a general equation of GEELEN[8] for relating a specific additive function A with the ring-number R_T and mol. weight M of saturated hydrocarbon mixtures

$$A = a + \frac{b + c\,R_T}{M} \quad \ldots\ldots\ldots\ldots\ldots \quad (64)$$

in which A represents a specific function ($r^{20}_{\text{spec.}}$, $\frac{\sigma^{\frac{1}{4}}}{d}$, $\frac{1}{d}$, etc.) and a, b and c are constants.

The specific refraction *vs.* $\frac{1}{M}$- and the specific parachor *vs.* $\frac{1}{M}$-diagrams of WEBER *et al.* were extended according to equation (64) to bicyclic naphthenes, tricyclic naphthenes, etc. (*cf.* Figs. 59 and 60).

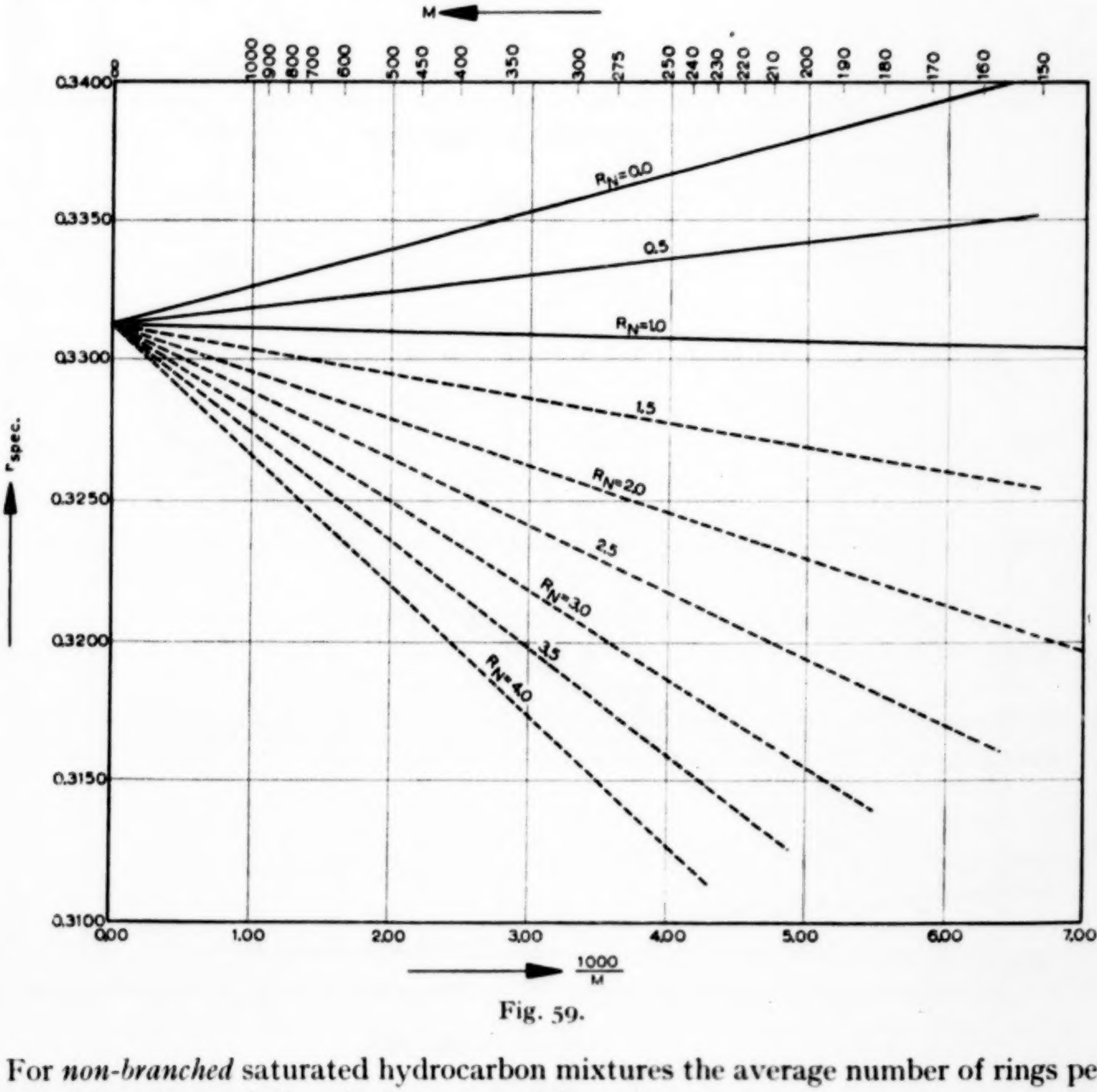

Fig. 59.

For *non-branched* saturated hydrocarbon mixtures the average number of rings per molecule can be read directly from one of these diagrams.

Chain branching causes a lowering of both the specific refraction and the specific parachor of saturated hydrocarbons, which corresponds, according to WEBER[35], with

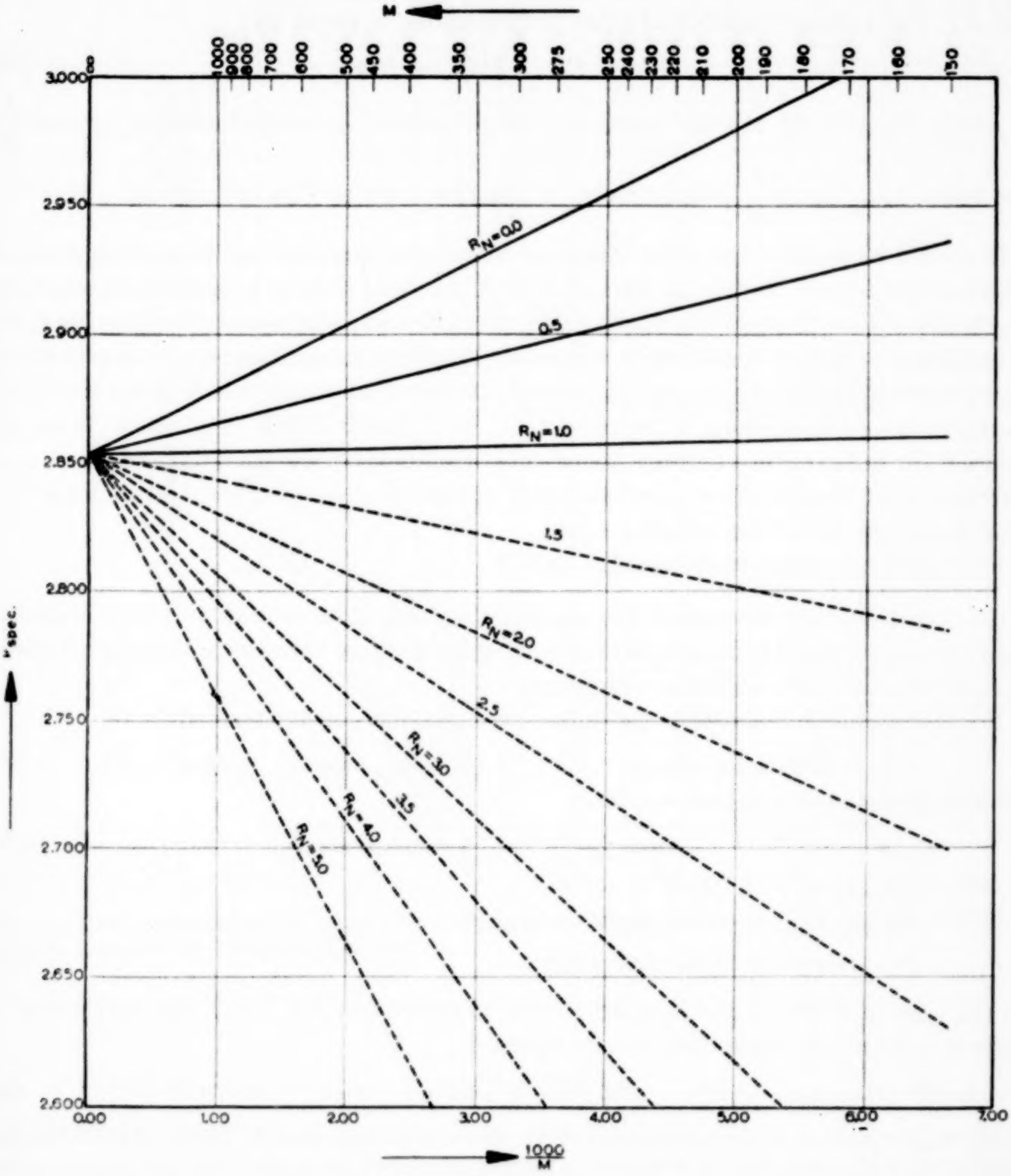

Fig. 60.

Figs. 59 and 60. Diagrams representing specific refraction *vs.* $\frac{1}{M}$ and specific parachor *vs.* $\frac{1}{M}$, based on A.P.I. data of *n*-alkanes, *n*-alkyl-cyclopentanes and *n*-alkyl-cyclohexanes at 20°C[9].

approx. 0.05 rings per branching unit in the specific refraction *vs.* $\frac{1}{M}$-diagram and with approx. 0.14 rings per branching unit in the specific parachor *vs.* $\frac{1}{M}$-diagram. Approximatively the degree of branching φ follows from the equation

$$\varphi = 10\,(R_T^p - R_T^r) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (65)$$

and R_T, the average number of rings per molecule, is given by

$$R_T = R_T^r - \tfrac{1}{2}(R_T^p - R_T^r) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (66)$$

in which R_T^r and R_T^p are the apparent ring-numbers estimated from $r_{\text{spec.}}$ and $\frac{1}{M}$, and from $p_{\text{spec.}}$ and $\frac{1}{M}$, respectively, in the diagrams of Figs. 59 and 60.

It should be pointed out that this method for ring analysis and branching analysis is based exclusively on reliable data of n, d, M and σ of pure individual hydrocarbons, and holds, within the limits of accuracy of the determination, for widely differing types of branched as well as non-branched saturated hydrocarbon mixtures. It is particularly recommended for the structural analysis of saturated polymers, where other statistical methods (n-d-M-method, ν-n-d-method, etc.) fail because they have been developed for mineral oils, and are based on correlations of physical data of mineral oil fractions that always show approximately the same small degree of branching: 1–2 branchings per molecular weight = 100.

Examples are given in Tables III and IV.

(*iv*) DE BOOIJS[29] correlated the parachor values of branched and non-branched heptanes and octanes to form equations analogous to those based on molecular magneto-optical rotation and molecular refraction.

For *paraffinic hydrocarbons* the following equation can be derived:

$$\varphi = 0.402\,(P_{n\text{-alkane}} - P) - 5.75\,(r_{\text{mol.}(n\text{-alkane})} - r_{\text{mol.}}) \quad . \; . \; . \quad (67)$$

for *hydrogenated mineral oil fractions*:

$$\varphi = 0.186\,(P_{n\text{-alkane}} - P) - 2.84\,(r_{\text{mol.}(n\text{-alkane})} - r_{\text{mol.}}) \quad . \; . \; . \quad (68)$$

in which $P_{n\text{-alkane}} = 2.852M + 25.22$,

$r_{\text{mol.}(n\text{-alkane})} = 0.3309M + 1.424$,

M = average molecular weight.

In the case of *aromatic fractions* an empirical correction for $\%C_A$, the percentage of carbon in aromatic structure, can be applied:

$$\varphi = 0.186\,(P_{n\text{-alkane}} - P) - 2.84\,(r_{\text{mol.}(n\text{-alkane})}) - r_{\text{mol.}}) - 0.00126\,M\cdot\%\,C_A. \quad (69)$$

With this equation a simple approximate determination can be made of φ in natural mineral oil fractions of not too extreme aromatic character ($\%C_A < 30\%$). The above-mentioned correction was obtained by comparing the parachor values of a large number of aromatic mineral oil fractions with those of the corresponding hydrogenated fractions.

It can easily be shown that the formulas for the determination of φ can also be represented graphically by using the specific refraction $r_{\text{spec.}}$ $(= \frac{r_{\text{mol.}}}{M})$ and the specific parachor p $(= \frac{P}{M})$ and plotting the function

$$\frac{p - 2.852 + 0.00375\%C_A}{r_{\text{spec.}} - 0.3309 - 0.0002\%C_A} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (70)$$

versus the total number of rings per molecule R_T (*cf.* Fig. 61).

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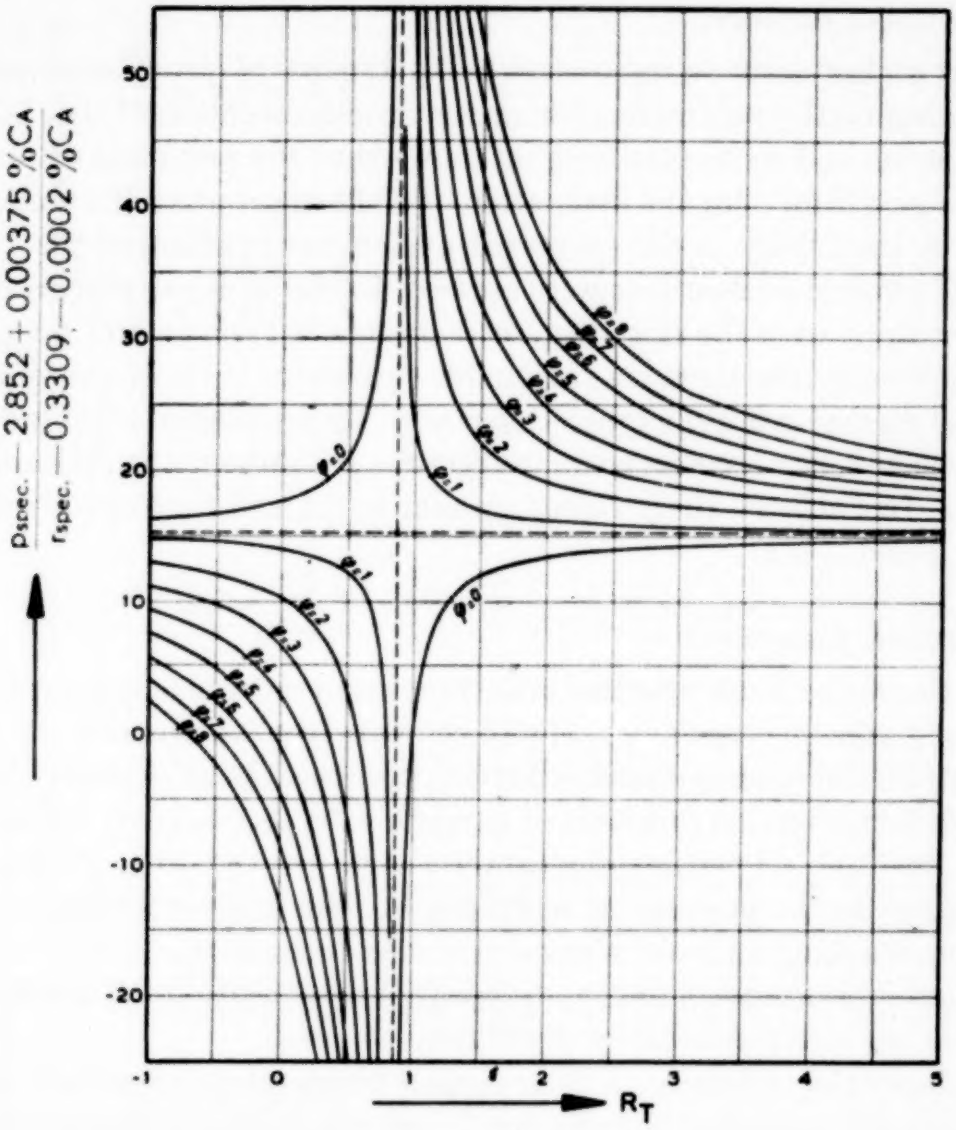

Fig. 61. Determination of the degree of branching φ in mineral oil fractions from specific refraction specific parachor and ring-number R_T.

e. Applications

(*i*) *Mineral oil fractions*

In Table III are collected data concerning a number of fractions of a Rumanian crude[37], before and after complete hydrogenation. It can be concluded that the results of the different methods for branching analysis show qualitatively the same picture. The number of branchings is relatively small and does not differ very much for the different fractions. This holds for a large number of crudes of different origin[29]. Therefore it is possible to determine the surface tension σ of natural and hydrogenated mineral oil fractions from n, d and ν (*cf.* Section II, 3, p. 439).

In the case of aromatic fractions it is generally impossible to measure the Verdet constant owing to the considerable absorption of visible light by even slightly coloured liquids. Therefore in non-hydrogenated fractions only parachor measurements can serve to determine the degree of branching. As follows from Table III, there is a reasonable agreement between the values of φ for hydrogenated and non-hydrogenated fractions.

(ii) Saturated liquid polymers

Table IV contains data on hydrogenated polymers of propylene, isobutene and cyclohexene obtained by polymerization under various conditions[38]. The Direct Method (ultimate analysis and molecular weight) shows that the polymers of propylene and isobutene are paraffinic; for the estimation of φ the appropriate formulas were used. In the case of the highly cyclic saturated cyclohexene-polymers the formulas for hydrogenated mineral oil fractions were applied. In the table are also given values of φ and R_T determined with the ring analysis diagrams of Figs. 59 and 60 (p. 458–459).

For these polymers also there is a reasonable agreement between the values of N_{CH_3}, the number of methyl groups per molecule, and φ, the number of alkyl groups minus 1.

If in the cyclohexene polymers no methyl groups are present then φ should approach the value —1. In Table IV the φ values amount to 0.2 and 1.3 respectively; the N_{CH_3} values are 0.3 and —0.2.

(iii) Isomerization phenomena

Although the methods discussed for branching analysis have only a semi-quantitative character, they may be especially useful in comparative experiments, *e.g.* for selecting optimal reaction conditions for isomerization processes. As an example data are given in Table V on isomerization products of paraffin wax, processed on a semi-commercial scale with a Pt–Al_2O_3–Cl platforming catalyst at 52 ata and different temperatures in the vapor phase (in the presence of hydrogen)[35]. The main reactions in this process are branching, cracking and to a minor extent also cyclization.

The reaction products were first hydrogenated to saturate small amounts of olefins, and then split up into fractions by distillation *in vacuo*.

Table V shows the influence of the reaction temperature especially in connection with the course of isomerization reactions: higher reaction temperatures favour the process of branching.

5. DETERMINATION OF MONO- AND DI-AROMATICS IN MINERAL OILS

a. Introduction

The application of several methods for structural analysis of mineral oils is, in general, limited to those fractions in which no structural elements are present in larger quantities than normally occur in mineral oil fractions. In highly aromatic concentrates, for instance, the normal analytical methods (*n–d–M; v–n–d*) may give inaccurate results, because different types of aromatics may influence the physical constants of the oil differently.

The development of newer techniques (chromatography, thermodiffusion) for the separation of the different groups of hydrocarbons from mineral oil fractions allows a better characterization of such "type-concentrates" with the aid of physical constants. Combination of physical methods of separation with the statistical analysis of the products obtained, may lead to a more detailed and more complete knowledge of the composition of oils.

By a simple percolation through silicagel a sharp separation into non-aromatic and aromatic compounds is achieved. By the same percolation approximate separations into mono-, di- and tri-aromatics have been obtained[39,40]. The result is a semi-quan-

TABLE V

BRANCHING ANALYSIS OF HYDROGENATED PLATFORMING PRODUCTS OBTAINED BY HYDROISOMERIZATION OF PARAFFIN WAX

Product	Result of vacuum distillation		Physical constants				Specific refraction	Specific parachor	Apparent ring-number estimated from		$\varphi = 11 \times \Delta ring$
	fraction	weight %	n_D^{20}	d_4^{20}	M	σ^{20} dyne/cm	r_D^{20}	p^{20}	r_D^{20} and M (Fig. 57)	p^{20} and M (Fig. 58)	
Starting material paraffin wax	1	5.6	1.4269	0.7642	315	25.3	0.3359	2.935	0.12	0.1	0.1
	2	15.7	1.4273	0.7645	325	25.4	0.3360	2.936	0.13	0.14	0.1
	3	17.7	1.4288	0.7675	340	25.8	0.3358	2.937	0.13	0.14	0.1
	4	20.6	1.4306	0.7718	362	26.1	0.3351	2.929	0.14	0.15	0.1
	5	16.9	1.4328	0.7750	396	26.5	0.3352	2.928	0.16	0.17	0.1
	6	23.3	1.4364	0.7826	467	27.0	0.3343	2.913	0.21	0.20	—0.1
Starting material paraffin wax, platformed at 410°C, 52 ata, contact time 10 sec	1	15.4	1.4241	0.7599	287	24.8	0.3359	2.937	0.21	0.23	0.2
	2	19.0	1.4283	0.7666	347	25.5	0.3358	2.931	0.09	0.18	1.0
	3	16.8	1.4299	0.7698	355	25.6	0.3355	2.922	0.15	0.30	1.7
	4	19.3	1.4319	0.7734	365	26.3	0.3353	2.928	0.16	0.20	0.4
	5	29.5	1.4354	0.7807	459	26.8	0.3345	2.914	0.21	0.30	1.0
Starting material paraffin wax, platformed at 420°C, 52 ata, contact time 10 sec	1	12.7	1.4221	0.7562	271	24.0	0.3361	2.927	0.23	0.39	1.8
	2	15.4	1.4280	0.7663	341	25.4	0.3357	2.930	0.13	0.21	0.9
	3	16.7	1.4294	0.7688	349	25.6	0.3356	2.926	0.14	0.25	1.2
	4	19.7	1.4310	0.7722	376	25.9	0.3352	2.921	0.17	0.28	1.2
	5	18.0	1.4329	0.7758	392	26.2	0.3349	2.916	0.20	0.34	1.5
	6	17.5	1.4363	0.7828	460	26.5	0.3342	2.898	0.29	0.60	3.4
Starting material paraffin wax, platformed at 435°C, 52 ata, contact time 10 sec	1	8.8	1.4119	0.7376	193	21.8	0.3373	2.929	0.28	0.50	2.4
	2	12.6	1.4258	0.7641	302	24.5	0.3352	2.912	0.32	0.52	2.2
	3	16.9	1.4286	0.7685	314	24.9	0.3352	2.907	0.30	0.56	2.9
	4	24.7	1.4295	0.7702	336	25.2	0.3351	2.909	0.28	0.51	2.5
	5	17.3	1.4319	0.7757	373	25.6	0.3343	2.900	0.39	0.61	2.4
	6	19.7	1.4356	0.7819	406	25.9	0.3341	2.885	0.40	0.85	5.0

titative determination of the weight percentages of 1 ring and 2 ring aromatics in distillation fractions of crude oils. A further separation of the molecules according to their ring-number is possible by thermal diffusion of the fractions obtained by percolation[41].

Along these lines a more or less complete separation is possible of paraffins, naphthenes with 1 ring, 2 rings, etc., benzene derivatives, mono-aromatics with 1 ring, 2 rings, etc., as shown in Table VI. The physical data for each fraction enable the corresponding amounts of structural compounds present to be calculated, as will be discussed below.

TABLE VI

TYPE ANALYSIS OF A BORNEO CRUDE OIL FRACTION (MOL. WT. 267) BY CHROMATOGRAPHIC SEPARATION AND THERMODIFFUSION[40]

Type	*Non-aromatic*	*Mono-aromatic*	*Di-aromatic*	*Tri-aromatic*	*Total*
Non-cyclic	2	—	—	—	2
Monocyclic	10	1	—	—	11
Dicyclic	7	2	6	—	15
Tricyclic	12	9	18	7	46
Tetracyclic	7	8	7	—	22
Pentacyclic	1	1	2	—	4
Total	39	21	33	7	100

GEELEN[8] investigated the influence of mono-aromatic and di-aromatic rings on several physical constants of mineral oils.

He considered as *mono-aromatics* molecules with one or more non-condensed benzene nuclei, *e.g.* alkyl-benzenes, tetralin-derivatives, diphenyl. *Di-aromatics* he defined as molecules with one or more naphthalene nuclei not condensed with each other or with a benzene nucleus.

GEELEN especially examined several specific functions (specific refraction r, specific sound velocity u, specific volume $1/d$). The use of these functions together with the hydrogen content (%H) enables the structural composition of aromatic hydrocarbons to be determined. From data on homologous series of pure mono- and di-aromatic hydrocarbons[36] he deduced the following equations for r, d and %H (20°C):

$$r = 0.3310 + \frac{1}{M}\,(1.419 - 1.654\ R_N + 0.76\ R_A{}^{\mathrm{I}} - 0.38\ R_A{}^{\mathrm{II}}) \quad . \ . \ (71)$$

$$\frac{1}{d} = 1.1747 + \frac{1}{M}\,(27.56 - 16.32\ R_N + 28.9\ R_A{}^{\mathrm{I}} + 26.9\ R_A{}^{\mathrm{II}}) \quad . \ . \ (72)$$

$$\%\mathrm{H} = 14.37 + \frac{1}{M}\,(172.6 - 172.6\ R_N + 690\ R_A{}^{\mathrm{I}} + 604\ R_A{}^{\mathrm{II}}) \quad . \ . \ (73)$$

where M = molecular weight,
R_N = number of naphthenic rings per molecule,
$R_A{}^{\mathrm{I}}$ = number of mono-aromatic rings per molecule, *e.g.* $R_A{}^{\mathrm{I}} = 1$ for benzene and 2 for diphenyl,
$R_A{}^{\mathrm{II}}$ = number of aromatic rings per molecule present in di-aromatic hydrocarbons, *e.g.* $R_A{}^{\mathrm{II}} = 2$ for alkylnaphthalenes.

With these equations R_N, $R_A{}^{\text{I}}$ and $R_A{}^{\text{II}}$ can be calculated, when n, d, M and %H are given:

$$R_N = 1.95 + M\,(0.138\,\triangle r + 0.0876\,\triangle \frac{1}{d} - 0.00382\,\triangle \text{H}) \quad . \; . \; . \,(74)$$

$$R_A{}^{\text{I}} = -1.60 + M\,(0.632\,\triangle r - 0.129\,\triangle \frac{1}{d} + 0.00616\,\triangle \text{H}) \quad . \; . \; . \,(75)$$

$$R_A{}^{\text{II}} = 1.56 - M\,(0.762\,\triangle r - 0.123\,\triangle \frac{1}{d} + 0.00429\,\triangle \text{H} \quad . \; . \; . \,(76)$$

$$\begin{aligned} \text{where } \triangle r &= 0.3310 - r, \\ \triangle \frac{1}{d} &= 1.1747 - \frac{1}{d}, \\ \triangle \text{H} &= 14.37 - \%\text{H}. \end{aligned}$$

These formulas, which have been deduced for individual aromatic compounds, are also suitable for the characterization of aromatic mineral oil fractions, aromatic concentrates, etc., provided that only small amounts of tri-aromatics and higher aromatic compounds are present. For sulphur-containing oils the value of R_N should be corrected:

$$\triangle R_N = -0.001 M \cdot \%\,\text{S} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \,(77)$$

No corrections are necessary for $R_A{}^{\text{I}}$ and $R_A{}^{\text{II}}$.

b. Applications

(*i*) *Analysis of aromatic oil fractions*

According to GEELEN[8] usually approximately equal amounts of mono- and di-aromatic compounds are present in natural mineral oil fractions:

$$2\,R_A{}^{\text{I}} \approx R_A{}^{\text{II}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \,(78)$$

Thus the contributions of these compounds to the specific refraction r of the fractions cancel out [*cf.* eqn. (71)]; this is the reason that diagrams for the ring analysis of saturated mineral oil fractions based on specific refraction and molecular weight are also valid for the estimation of naphthenic rings in aromatic fractions (*cf.* p. 418).

For the analysis of highly aromatic oils (chromatographic concentrates, products of solvent extraction, distillation fractions of oil residues) where the ordinary analytical methods (n-d-M, v-n-d, etc.) fail, the formulas of GEELEN are of great value because they allow a reasonable type-analysis of these products. When tri-aromatics are present the equations do not hold exactly; however, in these cases also, the total number of aromatic rings is given in a good approximation by

$$R_A = R_A{}^{\text{I}} + R_A{}^{\text{II}}. \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \,(79)$$

As an illustration, some data on the analysis of type concentrates obtained by chromatographic separation of a "Kerex" kerosine extract, are given in Table VII.

It can be seen that the analytical results of both the methods mentioned in Table VII agree reasonably well for saturated fractions, which was to be expected; for the

TABLE VII

ANALYSIS OF SATURATED, MONO-AROMATIC AND DI-AROMATIC FRACTIONS OBTAINED BY CHROMATOGRAPHIC SEPARATION OF A "KEREX"

	n_D^{20}	d_4^{20}	r_D^0	Mol. wt.	%H	%S	$R_A{}^I$	$R_A{}^{II}$	R_N	R_T	R_A	R_T
							(according to	*Geelen)*			*(n, d, M)*	
Saturated* fraction	1.4546	0.8213	0.3301	206	14.04	—	0.08	0.04	0.94	1.06	0.09	1.07
Mono-aromatics	1.5071	0.8982	0.3314	181	10.95	0.03	0.73	0.33	0.55	1.61	0.77	1.64
Di-aromatics	1.5958	0.9940	0.3423	167	7.83	0.11	0.30	1.78	-0.01	2.07	1.91	1.55

* After elimination of oxygen compounds by percolation through Al_2O_3.

mono- and di-aromatic concentrates the results of the *n*-*d*-*M*-method show deviations in particular for R_T.

(*ii*) *Hydrogenation of aromatic mineral oil fractions*

The analytical hydrogenation is very important for the study of natural mineral oils.

VAN NES AND VAN WESTEN[42] described the physical constants and elementary composition of intermediates in the complete hydrogenation of a large number of mineral oil fractions. These data were used by GEELEN[8] to study the behaviour of mono- and di-aromatics during catalytic hydrogenation.

In Fig. 62 the course of the selective hydrogenation experiments is represented schematically in terms of the aromatic composition of the partially hydrogenated intermediates. Generally there is a pronounced selectivity in connection with the saturation of di- and mono-aromatic compounds: saturation of the latter does not occur to a significant degree before larger amounts of di-aromatics have been transformed by partial hydrogenation into the corresponding mono-aromatics.

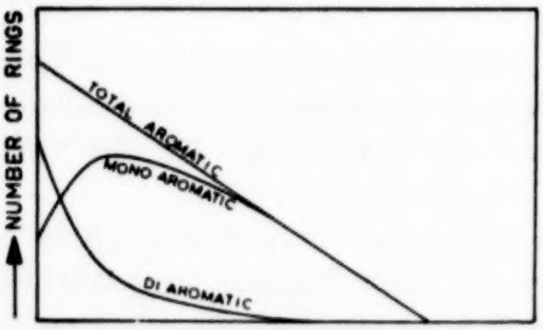

Fig. 62. Schematical representation of the analytical hydrogenation of a mineral oil fraction.

6. SULPHUR COMPOUNDS IN MINERAL OILS

Mineral oils contain, besides hydrocarbons, certain amounts of foreign elements, of which sulphur, nitrogen and oxygen are the most important ones. Whereas, in general, nitrogen and oxygen are present in very small quantities only, sulphur compounds may be present in larger quantities. Especially in recent years has the production of crudes with high sulphur contents (5% S and more) been increased and the significance of desulphurization processes in the petroleum technology is still gaining in importance.

The weight% of sulphur does not give an impression of the amount of sulphur compounds, that may be present. For example, with a sulphur content of 5% and an av. mol. wt. of 320 the mineral oil contains $5 \cdot \frac{320}{32} = 50\%$ sulphur compounds on an average, if it is assumed that in molecules that contain sulphur only one atom of sulphur is present.

It is of great value to know which types of sulphur compounds are present in a crude oil, because the various types may behave quite differently in respect to the properties of the crude and of the products that can be obtained from it by physical or chemical methods. According to recent investigations, in lower molecular oil fractions sulphur appears mainly in the form of alkane-thiols, cyclohexane-thiols and thioalkanes; in higher molecular fractions cyclic sulphur compounds of the thiophen type predominate.

In the case of statistical methods of analysis of sulphur-containing crude oil fractions one generally confines oneself to small corrections on the applied graphs or equations. These corrections, which have been estimated empirically, are valid only for small percentages of sulphur and do not take into account the nature of the sulphur compounds present in the fractions.

In recent years the intensive study of sulphur compounds, sponsored by several oil companies[43], has led to a collection of physical data on many of these compounds, which enables us to predict several properties of sulphur compounds not yet investigated[44,45].

VAN ZIJLL LANGHOUT developed graphs for compounds consisting of C, H and S, analogous to the graphical representation of C–H–O compounds of VAN KREVELEN[46]. These graphs, of which Fig. 63 is an example, are based on the ultimate analysis, and can be applied to identify pure sulphur compounds and to analyse simple mixtures

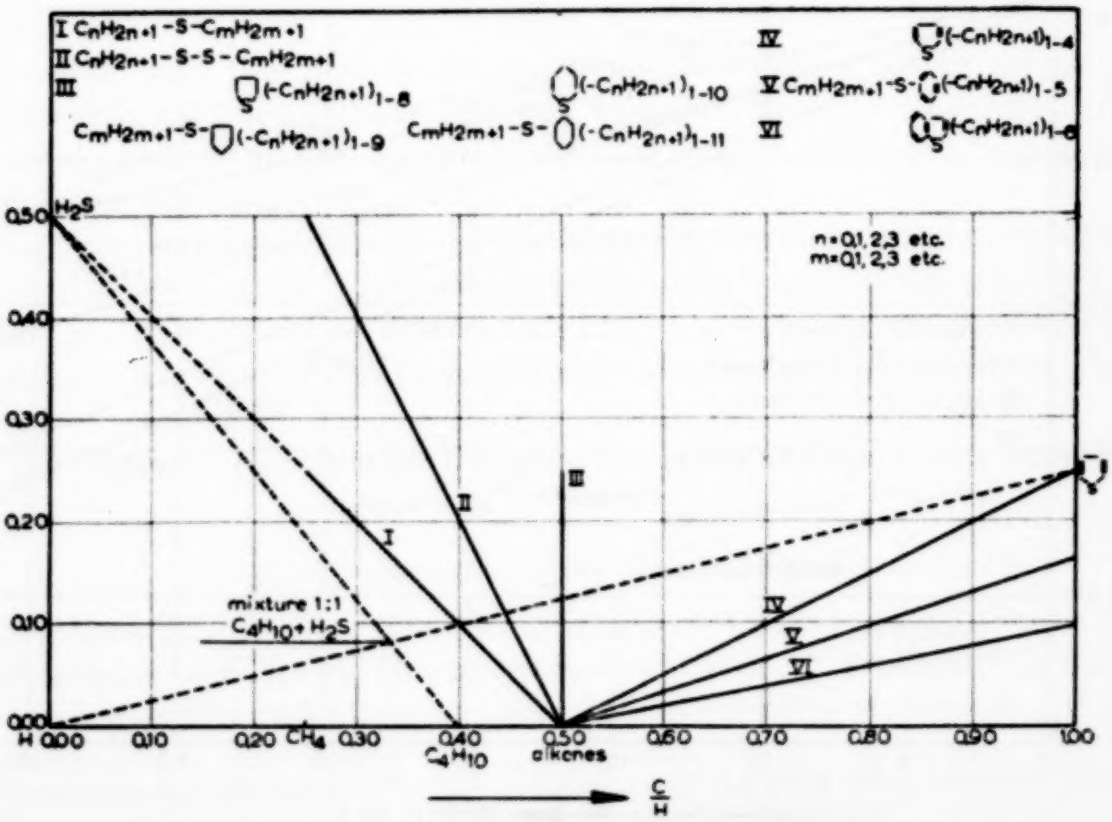

Fig. 63. Graphical analysis of sulphur compounds.

thereof; they are also useful to represent distinct chemical transformations in which sulphur compounds are involved.

The following examples may serve to illustrate the use of the graph:

(a) from H_2S (C:H = 0, S:H = 0.5) and C_4H_{10} (C:H = 0.4, S:H = 0) thiophen (C:H = 1.0, S:H = 0.25) can be obtained as the result of a dehydrogenation:

$$H_2S + C_4H_{10} \rightleftarrows C_4H_8S + 2\,H_2$$

(b) by the addition of H_2S (C:H = 0, S:H = 0.5) to alkenes (C:H = 0.5, S:H = 0) thiols are formed:

$$H_2S + C_nH_{2n} \rightleftarrows C_nH_{2n+1}SH$$

which are represented in the diagram by points on line I.

In Fig. 64 the *specific refraction* is plotted *versus* the weight percentage of sulphur. On the lines that represent different groups of sulphur compounds values of n_D^{20} are indicated, thus making an easy orientation possible. Similar graphs based on other physical constants can be constructed, permitting the prediction, by interpolation or extrapolation, of physical constants of still unknown members of homologous series of compounds. The accuracy and usefulness of these graphs will increase as more reliable physical constants become known.

These diagrams may also be useful for the characterization of sulphur compounds in crude oil fractions, provided that separation of the fractions into two parts, *i.e.* the hydrocarbons and the sulphur compounds, is possible. However, the sulphur compounds in mineral oils, especially those containing high percentages of carbon and hydrogen, resemble the corresponding hydrocarbons very closely, both physically and chemically. This greatly hampers their complete separation, although modern analytical techniques[47] have made considerable progress in this direction.

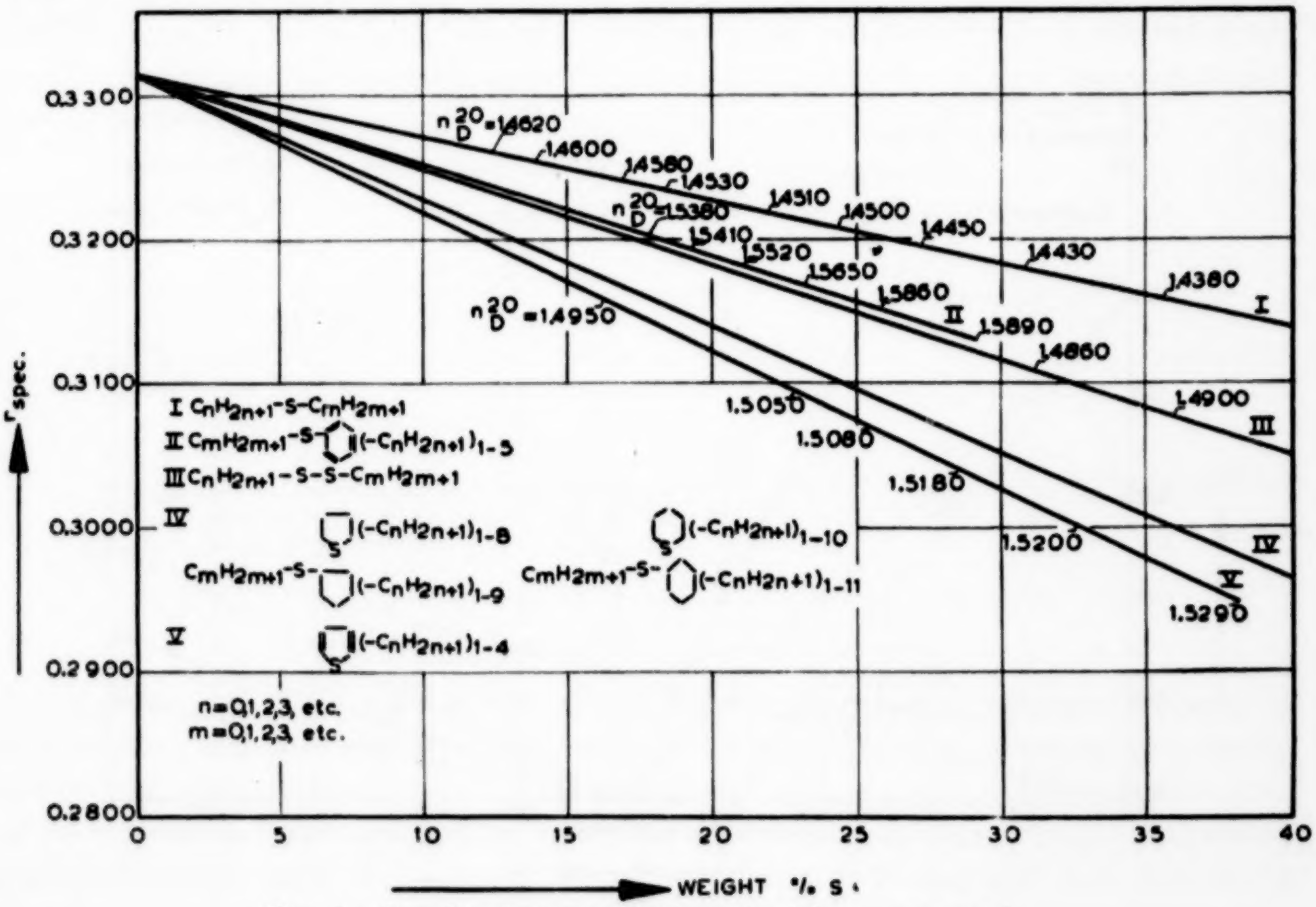

Fig. 64. Graphical representation of sulphur compounds.

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III. APPLICATION OF GRAPHICAL STATISTICAL METHODS IN THE DETERMINATION OF THE COMPOSITION OF GLASSES AND SILICONES

1. INTRODUCTION

In the last few years the graphical statistical methods have been successfully applied not only to petroleum, fatty oils and coal, but also to glass and silicones. Though the recently developed methods for glass and silicones are still in their initial stages, some remarkable results have already been obtained.

In order to develop methods that can be applied to glass, it is necessary to study homogeneous glasses with a known composition. To obtain a known composition the glass mass has to be dealt with in a *quantitative* way during the homogenizing process and much of the work to prepare the glass is done with this purpose in mind.

The method worked out by VAN LEEUWEN at the Department of Chemical Engineering of the Technological University of Delft, can be used to prepare homogeneous glasses with known composition.

Certain amounts of chemically pure oxides or in many cases the corresponding carbonates are weighed and intimately mixed in a platinum crucible. The mixture is *slowly* heated to 700°C* in the course of one day. In this period a reaction between the solid substances takes place and CO_2 is expelled. After this a porous cake has been formed, which stands free from the crucible wall and therefore contains the starting material quantitatively. Then it is possible to increase the temperature *quickly* to 1300°C*, in order to melt the glass without drops of glass being formed on the wall. This temperature, which is maintained for some hours, may neither be too high because of possible losses by evaporation, nor too low in order to ensure sufficient homogenization of the glass.

The crucible with the glass is quenched in cold water, a rubber stopper is put on the crucible and the glass is loosened from the inner wall by softy knocking with a small hammer on the outer wall. In this way the glass can be taken out of the crucible quantitatively.

The homogeneity of the glass can be checked by determining the density of some of the separate pieces of glass, which on inspection with a magnifying glass should not show small cracks. If the values of the density differ 0.0004 or less, the glass is considered to be homogeneous. In most cases it is necessary to repeat the melting of the glass once or twice after grinding.

After the preparation of the glass the refractive index and the density are measured.

a. Determination of the density of glass

For the determination of the density a small piece of glass is brought into a mixture of dibromoethane $Br\text{-}CH_2\text{-}CH_2\text{-}Br$ and bromoform $CHBr_3$**. The density of the former liquid is lower and that of the latter is higher than the density of the glass. At a certain temperature the proportion of these liquids is adjusted in such a way that the piece of glass neither sinks nor floats. Then the density of the liquid mixture is determined at the same temperature. This density is equal to the density of the glass.

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* This temperature is determined by the composition of the glass being prepared, and is only given as an example.

** The choice of the two liquids depends on the nature of the glass and on its density.

Care must be taken that no moisture is present in the dibromoethane and in the bromoform. This is especially important for glasses of which the surfaces are easily attacked by water. This presence of moisture may give rise to inaccurate results in the subsequent determination of the refractive index. For the same reason it is advisable to keep the pieces of glass stored in a desiccator.

b. Determination of the refractive index of glass

The refractive index is measured according to a method developed by FAICK AND FONOROFF[48]. The principle of the method can be described as follows.

A parallel, monochromatic beam of light is passed through a tube (Fig. 65) containing two adjustable knife-edge diaphragms A and B, each of which removes about one half of the light.

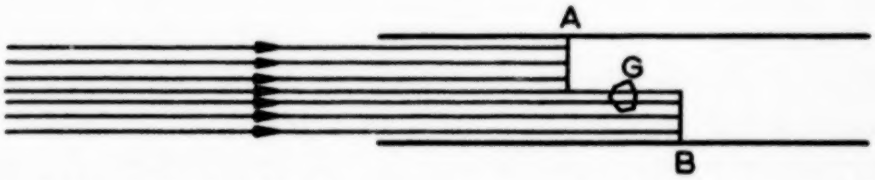

Fig. 65. Principle of the method of FAICK AND FONOROFF for measuring the refractive index of glass.

A cylindrical glass tube containing the immersion liquid and the piece of glass of which the refractive index has to be determined, is placed between the two diaphragms. The immersion liquid consists of petroleum ether (or dioxane) and α-chloronaphthalene. The temperature of the immersion liquid is controlled by circulating water around the tube.

If the refractive index of the glass is equal to that of the liquid, only dim light is allowed to pass along the two diaphragms.

If the refractive index of the glass is different from that of the liquid, light can be seen through a telescope placed to the right of B. This can be made clear as follows.

In Fig. 66 two cases are considered, namely I and II.

I. The refractive index n_1 of the immersion liquid is larger than the refractive

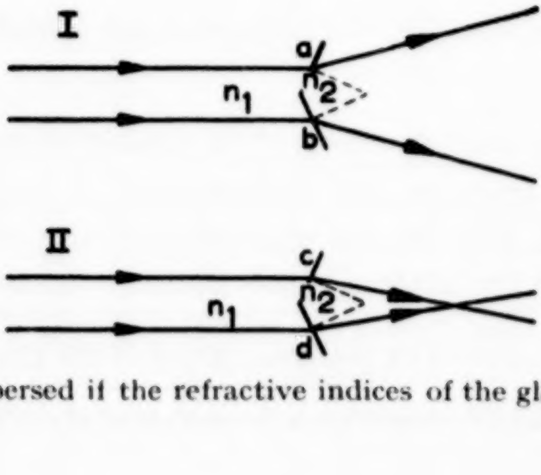

Fig. 66. How the light is dispersed if the refractive indices of the glass and the immersion liquid are different.

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index n_2 of the piece of glass ($n_1 > n_2$). Light falling on surface *a* can be seen through the telescope, light falling on surface *b* cannot be seen.

II. $n_1 < n_2$. Light falling on surface *d* can be seen through the telescope, light falling on surface *c* cannot be seen.

It can be concluded that if $n_1 \neq n_2$ light can be seen, whereas if $n_1 = n_2$ no light can be seen. The immersion liquid is adjusted so that this last condition is fulfilled. The refractive index of the immersion liquid is then determined at the same temperature by means of an Abbe refractometer. The value found is equal to the refractive index of the glass.

2. THE THERMAL BEHAVIOUR OF POTASSIUM AND SODIUM SILICATES

It is a well-known fact that the physical constants of glasses depend on the temperature to which the glass has been exposed[49]. This treatment can be carried out by keeping a small piece of the glass for a sufficient time at a certain constant temperature to obtain a constant value of the physical constants. At 600°C a few minutes may suffice, at 350°C hundreds of hours may be necessary. After this period the pieces of glass are either quenched in benzene at 6°C (if the glass has been exposed to a relatively low temperature) or in toluene at 100°C (if the glass has been treated at a relatively high temperature).

A few types of glasses have been investigated in this way. They were composed either of Na_2O and SiO_2 or of K_2O and SiO_2. Their composition is given in Table VIII.

TABLE VIII

COMPOSITION OF GLASSES J_1, F, K_1 AND K_2

Composition of glass	*Weight percentage of*			*Molecular percentage of*		
	SiO_2	*Na_2O*	*K_2O*	*SiO_2*	*Na_2O*	*K_2O*
J_1	71.38	28.62		72.03	27.97	
F	77.38	22.62		77.95	22.05	
K_1	72.31		27.69	80.37		19.63
K_2	78.58		21.42	85.18		14.82

The density of these glasses was determined after thermal treatment at different temperatures. The values of these densities for the different glasses are reported in Tables IX, X, XI and XII. The density values of the glasses have also been plotted as a function of the temperature of treatment in Figs. 67, 68, 69 and 70.

It appears that relatively low temperatures of treatment do not lead to a change in the density measured at 20°C. For the types of glass tested, from a certain temperature between 400°C and 450°C onwards there is a sharp fall in the density value until a temperature between 500°C and 650°C is reached. Beyond this temperature no further change takes place in the density value.

In Tables IX to XI the values of the refractive index, n_D^{20}, for a number of temperatures of treatment are also given. The specific refraction defined according to LORENTZ-LORENZ as $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}$, was calculated and the values obtained are also included in the tables. It is very remarkable that for a glass of definite composition the value

TABLE IX

THERMAL TREATMENT OF GLASS J_1

Temperature °C	d_4^{20}	n_D^{20}	$r_{spec.} = \frac{n^2-1}{n^2+2}\cdot\frac{1}{d}$
365	2.4557		
392	2.4556	1.5011	0.1200
414	2.4555		
430	2.4546		
458	2.4497	1.4997	0.1200
471	2.4476		
473	2.4473		
493	2.4453		
532	2.4443		
576	2.4442		

TABLE X

THERMAL TREATMENT OF GLASS F

Temperature °C	d_4^{20}	n_D^{20}	$r_{spec.} = \frac{n^2-1}{n^2+2}\cdot\frac{1}{d}$
360	2.4079		
387	2.4079	1.4940	0.1210
412	2.4076	1.4942	0.1210
438	2.4070		
483	2.4024		
539	2.3964		
586	2.3948		
602	2.3947	1.4921	0.1211

TABLE XI

THERMAL TREATMENT OF GLASS K_1

Temperature °C	d_4^{20}	n_D^{20}	$r_{spec.} = \frac{n^2-1}{n^2+2}\cdot\frac{1}{d}$
366	2.3887		
398	2.3885	1.4931	0.1217
452	2.3885		
495	2.3827		
513	2.3809		
547	2.3763		
593	2.3706		
623	2.3681		
663	2.3663		

of the *specific refraction* appears to be *independent* of the *temperature of treatment.*

It is furthermore interesting to note that in a specific refraction-composition diagram (Fig. 71) for the potassium- and sodium-silicate glasses studied, the points are

TABLE XII

THERMAL TREATMENT OF GLASS K_2

Temperature °C	d_4^{20}	n_D^{20}	$r_{spec.} = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}$
408	2.3500		
470	2.3496	1.4863	0.1223
487	2.3487		
500	2.3473	1.4860	0.1223
513	2.3452	1.4855	0.1223
541	2.3411	1.4852	0.1224
558	2.3403	1.4849	0.1224
575	2.3397		
588	2.3398		
615	2.3395		

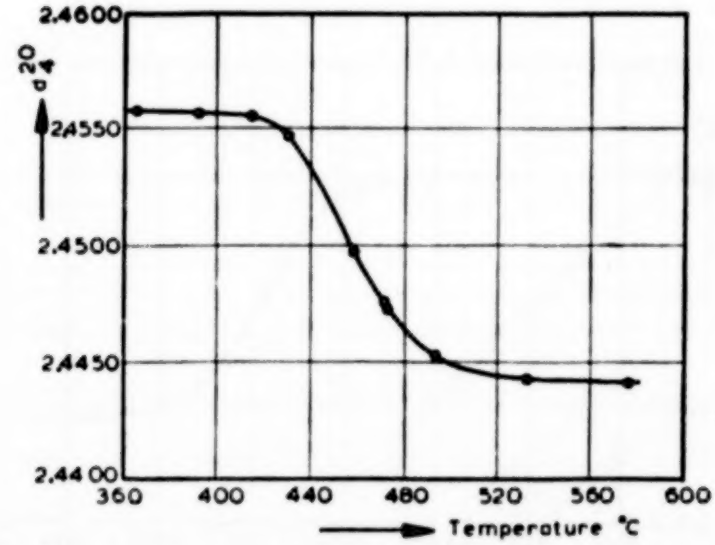


Fig. 67. The density of glass J_1 as a function of the temperature of treatment.

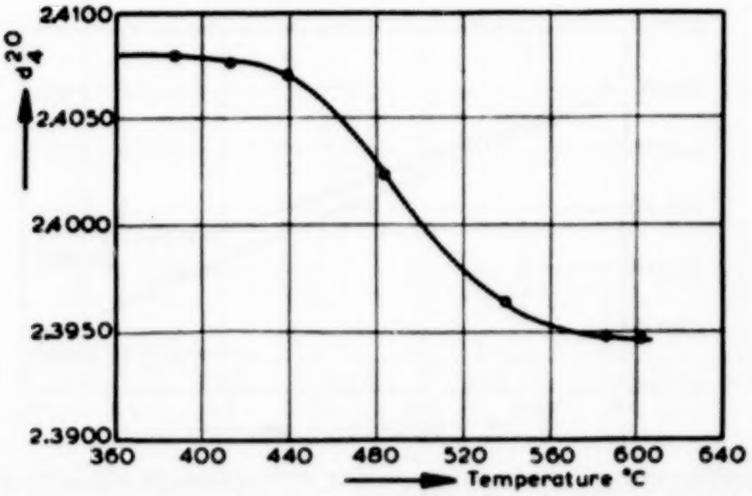


Fig. 68. The density of glass F as a function of the temperature of treatment.

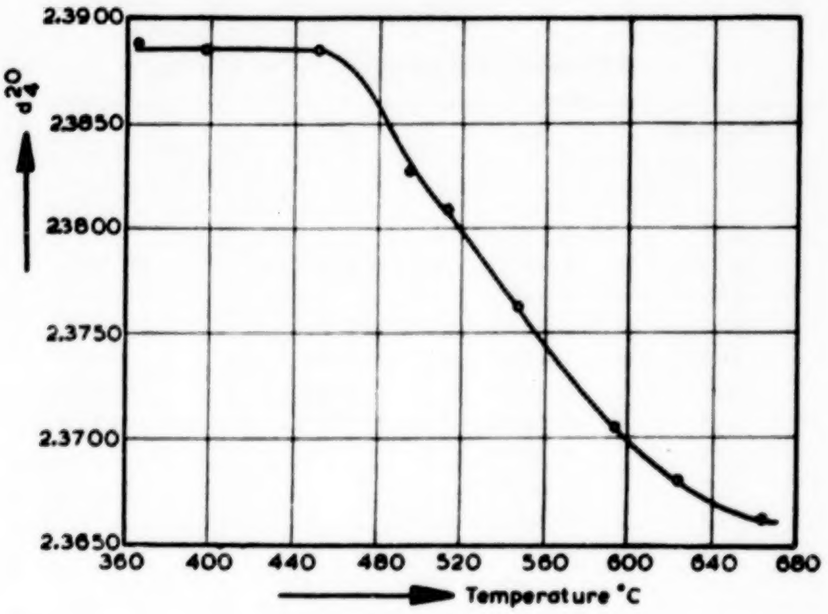


Fig. 69. The density of glass K_1 as a function of the temperature of treatment.

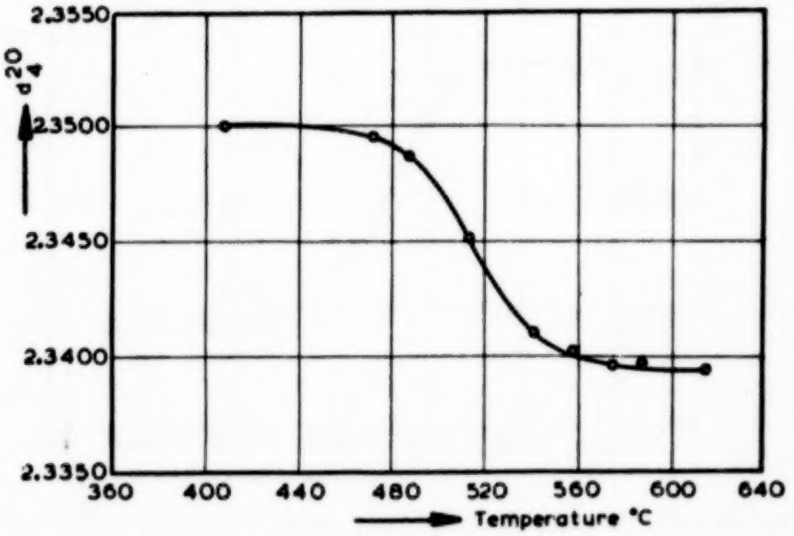


Fig. 70. The density of glass K_2 as a function of the temperature of treatment.

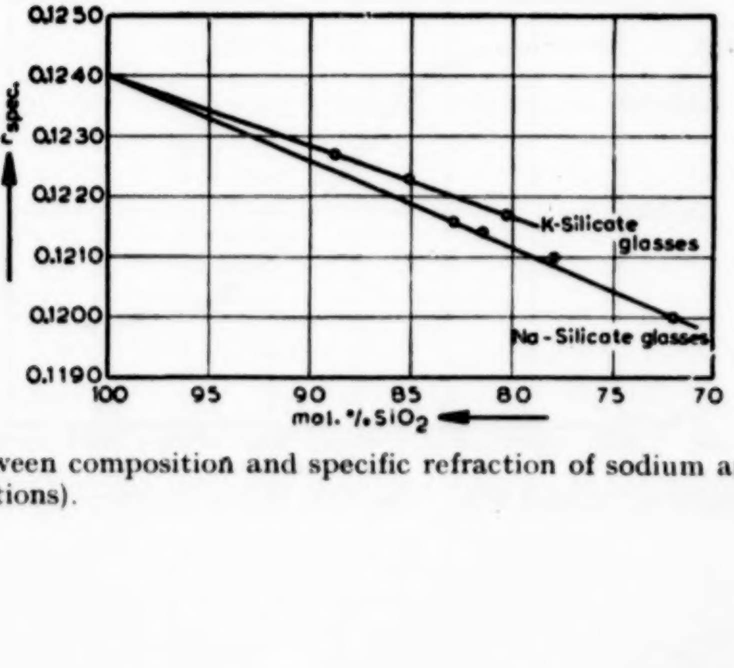


Fig. 71. Relation between composition and specific refraction of sodium and potassium silicate glasses (own preparations).

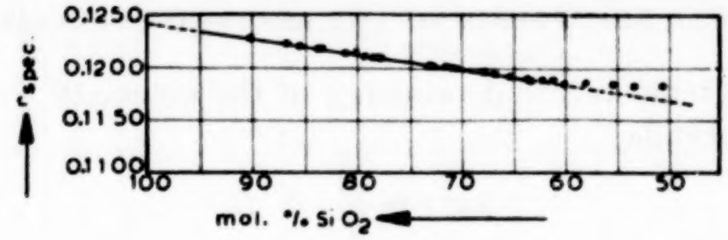


Fig. 72. Relation between composition and specific refraction of a large number of sodium silicates (prepared by different authors).

on two straight lines, which intersect at the specific refraction value of molten quartz. A reliable value of *r* of glassy quartz is given by SOSMAN[50].

The results obtained are in agreement with reliable values, which have been reported in the literature for Na_2O-SiO_2 glasses. These values are represented in Fig. 72.

The straight lines permit the determination of the composition of potassium and sodium glasses by determining their density and refractive index and calculating their specific refraction.

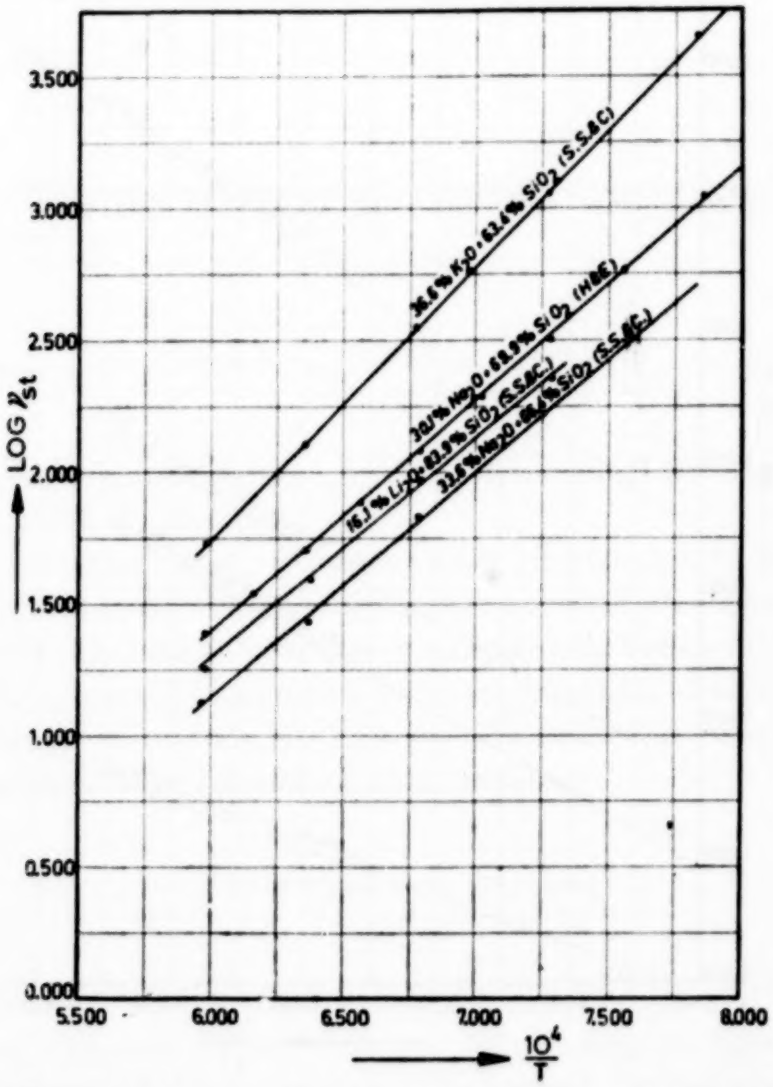


Fig. 73. Log ν – $\frac{1}{T}$ graph for some K_2O-SiO_2, Li_2O-SiO_2 and Na_2O-SiO_2 glasses.

3. TEMPERATURE DEPENDENCE OF THE KINEMATIC VISCOSITY OF GLASSES

On studying the temperature dependence of the kinematic viscosity of glasses it appears that the formula

$$\log \nu = \frac{A}{T^x} + B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

discussed in Section II, 3, not only holds for liquid hydrocarbons and their mixtures (natural or synthetic), water, molten metals, sugar and sulfuric acid solutions in water and for silicones, but also for molten glasses[92]. To investigate the validity of formula (45) in this field, data have been used that have recently been published by HEITKAMP AND ENDELL[51], SHARTSIS, SPINNER AND CAPPS[52] and LILLIE[53]. For these glasses $\log \nu = f(\frac{1}{T^x})$ graphs were constructed[49], the value of x being calculated as described previously (Section II). Some of these graphs are given in Figs. 73, 74, 75 and 76.

It appears that the value of x varies from 1 to 3 for the different glasses. The accuracy with which x can be determined is a few units in the first decimal place, owing to the

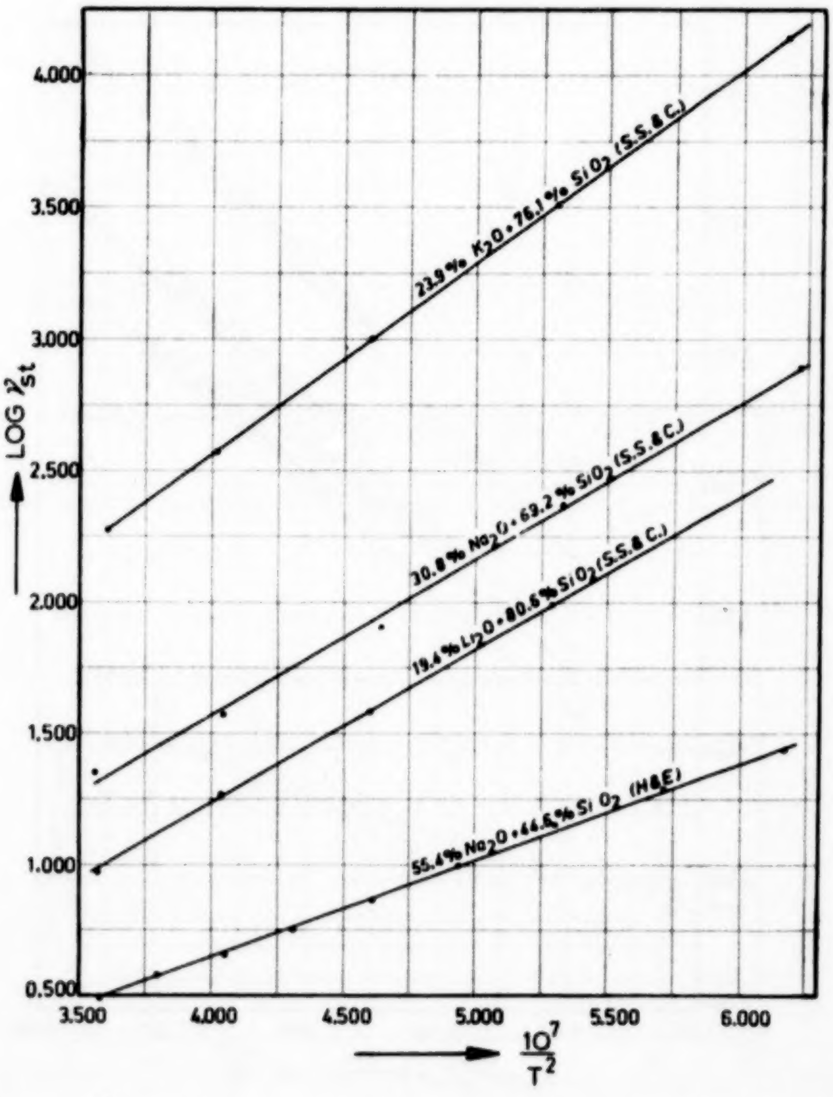


Fig. 74. Log $\nu - \frac{1}{T^2}$ graph for some K_2O-SiO_2, Li_2O-SiO_2 and Na_2O-SiO_2 glasses.

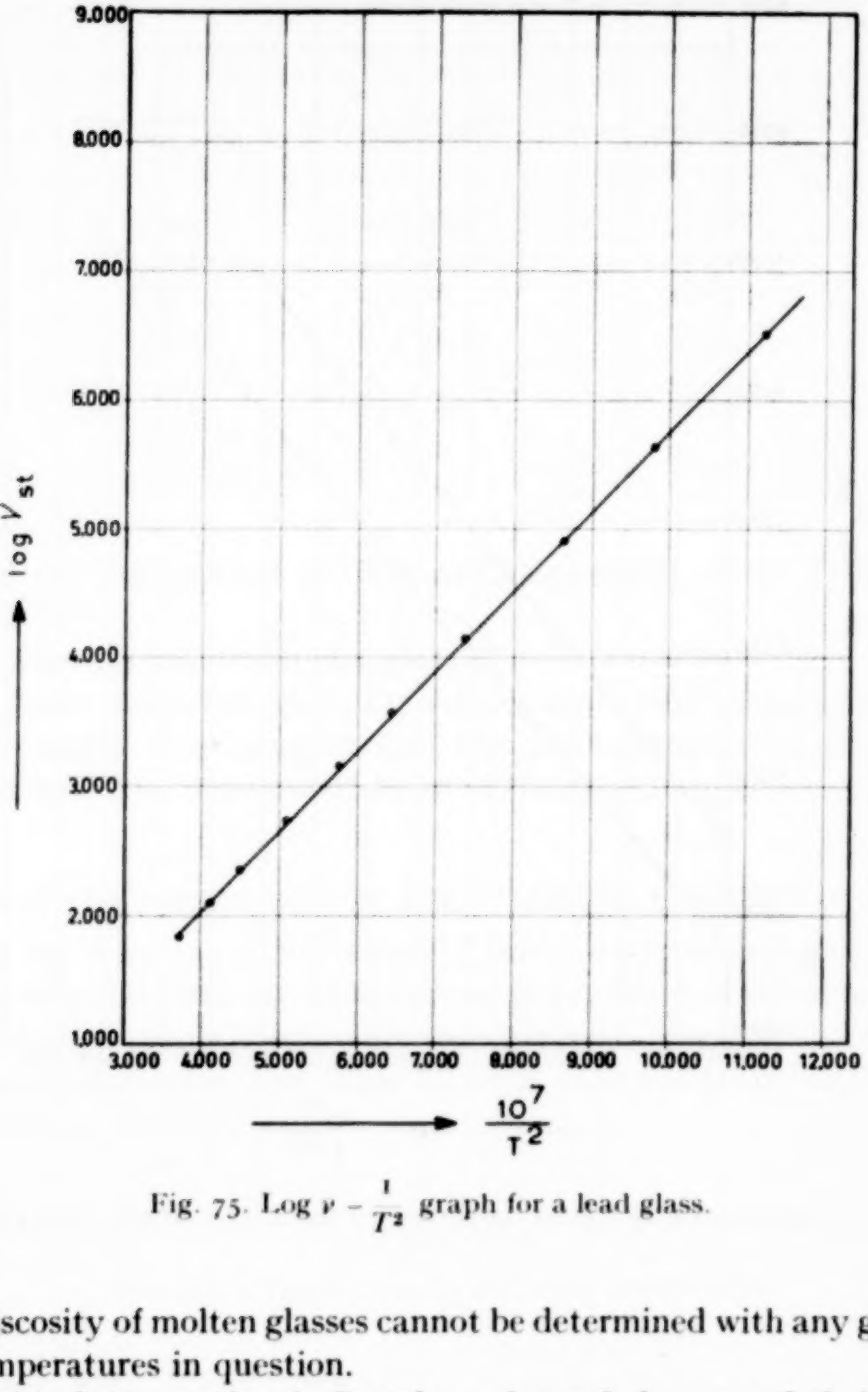


Fig. 75. Log $\nu - \frac{1}{T^2}$ graph for a lead glass.

fact that the viscosity of molten glasses cannot be determined with any great accuracy at the high temperatures in question.

The relationship between the A, B and x values of glasses and their composition is not yet clear, in contrast to the relationship between x and the composition of saturated mineral oil fractions. The lack of accuracy of x apparently hampers the establishment of this relationship for glasses. This can only be an incitement to determine the viscosity of glasses with greater precision than has been possible so far, thus enabling the x values in the case of the glasses to be calculated more precisely.

4. THE STRUCTURE OF SILICONES

Silicones are polymeric compounds in which molecules with -Si-O-Si-O- bonds occur, organic groups being attached to the Si-atoms. Many silicones have found practical application, the particular application being dependent on the chemical structure. HUNTER, HYDE, WARRICK AND FLETCHER[54] found regularities in the case of some cyclic

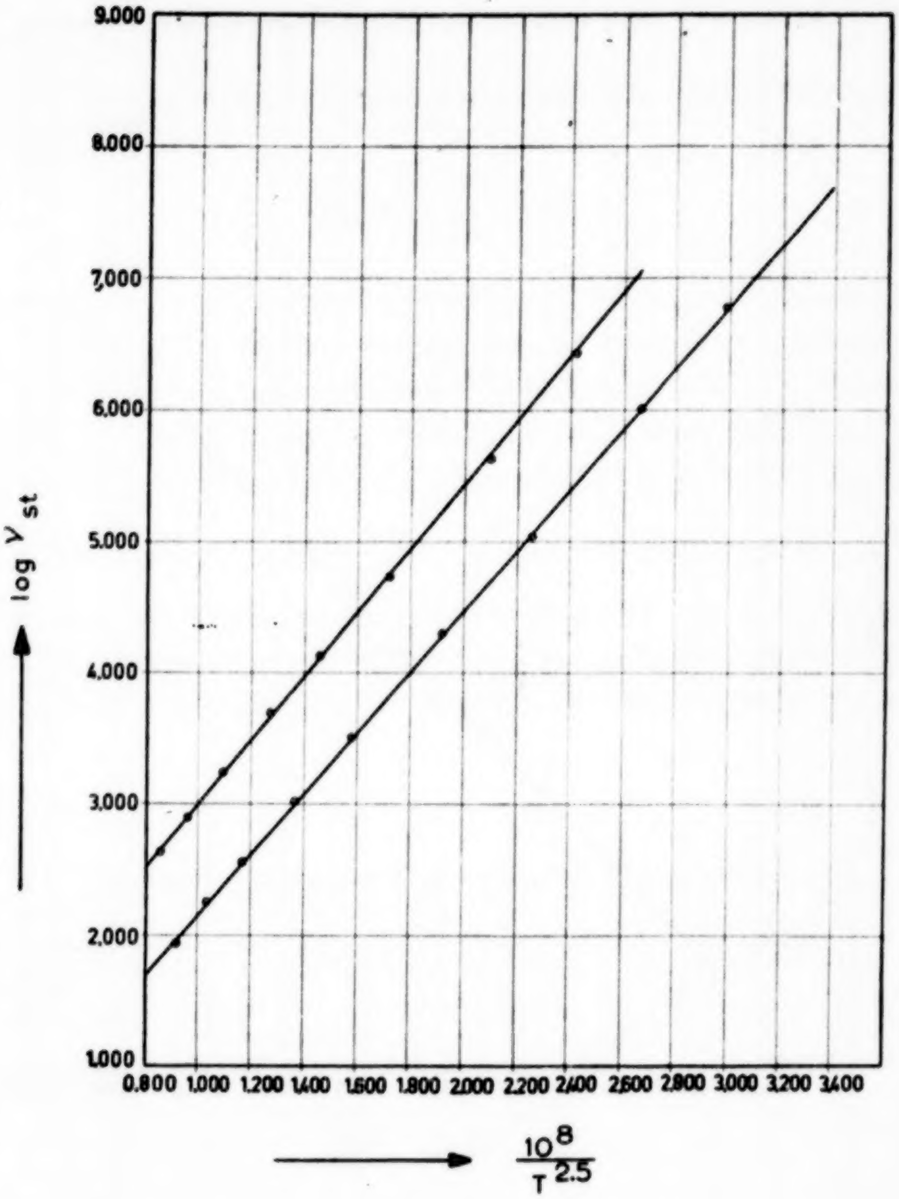


Fig. 76. Log ν – $\frac{1}{T^{2.5}}$ graph for a B_2O_3 glass (upper curve) and a $Na_2O-CaO-SiO_2$ glass (lower curve).

silicones, of which several physical constants have been measured. Of these, the refractive index, density, surface tension (all at 25°C) and the derived functions, specific refraction according to LORENTZ-LORENZ $\left(\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}\right)$ and specific parachor $\frac{\sigma^{1/4}}{d}$, are collected in Table XIII.

It appears that for these cyclic polymers the values of the specific refraction and the specific parachor are almost constant, though the refractive index, the density and the surface tension vary notably. The specific refraction and the specific parachor are independent of the degree of polymerization.

Although this result is only the first step in establishing relationships between chemical structure and physical constants of silicones, it is very promising. New investigations with the aim of establishing new relationships have been started in the

TABLE XIII

PHYSICAL CONSTANTS OF CYCLIC SILICONES

	Tetramer $[(CH_3)_2SiO]_4$	*Pentamer* $[(CH_3)_2SiO]_5$	*Hexamer* $[(CH_3)_2SiO]_6$	*Heptamer* $[(CH_3)_2SiO]_7$
d_4^{25}	0.9497	0.9531	0.9613	0.9664
n_D^{25}	1.3935	1.3958	1.3996	1.4018
σ^{25}	17.37	17.42	17.61	18.30
$\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}$	0.2512	0.2516	0.2515	0.2514
$\frac{\sigma^{1/4}}{d}$	2.145	2.140	2.130	2.140

laboratories of the Department of Chemical Engineering of the Technological University at Delft[93].

It must be borne in mind that, for glass of a certain composition, the specific refraction according to LORENTZ-LORENZ is independent of the temperature of treatment. The results discussed above suggest that this phenomenon may also be connected with polymerization and depolymerization of the glass in question.

5. TEMPERATURE DEPENDENCE OF THE KINEMATIC VISCOSITY OF SILICONES

This subject has been treated in Section II, but more details are given here.

We have already discussed the temperature dependence of the kinematic viscosity of silicones with relatively large viscosity values (silicone lubricants). The silicones concerned are chain polymers and in Table XIV the values of their F.V.T.I. is given together with their ν_{20} and x values.

TABLE XIV

VISCOSITY PROPERTIES OF SILICONE LUBRICANTS

Silicone fluid	ν_{20} *in cs*	*F.V.T.I.* = $\log \frac{\nu_{20}}{\nu_{70}}$	x
A	64.83	0.368	1.0
B	143.1	0.371	1.1
C	410.2	0.375	0.7
D	1393	0.378	0.9
E	6400	0.370	0.8

The F.V.T.I. values prove to be practically constant, *viz.* 0.37 to 0.38, which means that (since x is almost equal to 1) the temperature dependence for these silicone oils is practically the same for the whole viscosity range from 65 to 6400 cs.

This is not the case for lower viscosity values of the same series of silicones and for cyclic polymers. Viscosity values at 20°C, F.V.T.I. and x values of both these groups are given in Table XV.

TABLE XV

VISCOSITY PROPERTIES OF SILICONES

Compound		*Indicated in Fig. 77 as*	*log ν_{20}*	*log $\frac{\nu_{20}}{\nu_{70}}$ F.V.T.I.*	*x*
Cyclic polymers					
$[(CH_3)_2SiO]_3$	cyclic trimer	D 3	0.018*	0.289*	1.7*
$[(CH_3)_2SiO]_4$	cyclic tetramer	D 4	0.405	0.347	1.5
$[(CH_3)_2SiO]_5$	cyclic pentamer	D 5	0.638	0.377	1.3
Linear polymers					
$(CH_3)_3Si\text{-}O\text{-}Si(CH_3)_3$	hexamethyldisiloxane	MM	−0.178	0.204	1.1
MS 200/ 1 cs	commercial product	MS 200/1	0.038	0.230	1.1
MS 200/ 2 cs	commercial product	MS 200/2	0.346	0.275	1.0
MS 200/ 3 cs	commercial product	MS 200/3	0.542	0.297	0.9
MS 200/ 5 cs	commercial product	MS 200/5	0.764	0.316	1.1
MS 200/10 cs	commercial product	MS 200/10	0.893	0.323	1.1

* Extrapolated.

It appears that for the silicones given in Table XV the F.V.T.I. is no longer a constant. In Fig. 77 the F.V.T.I. is plotted against log ν_{20}.

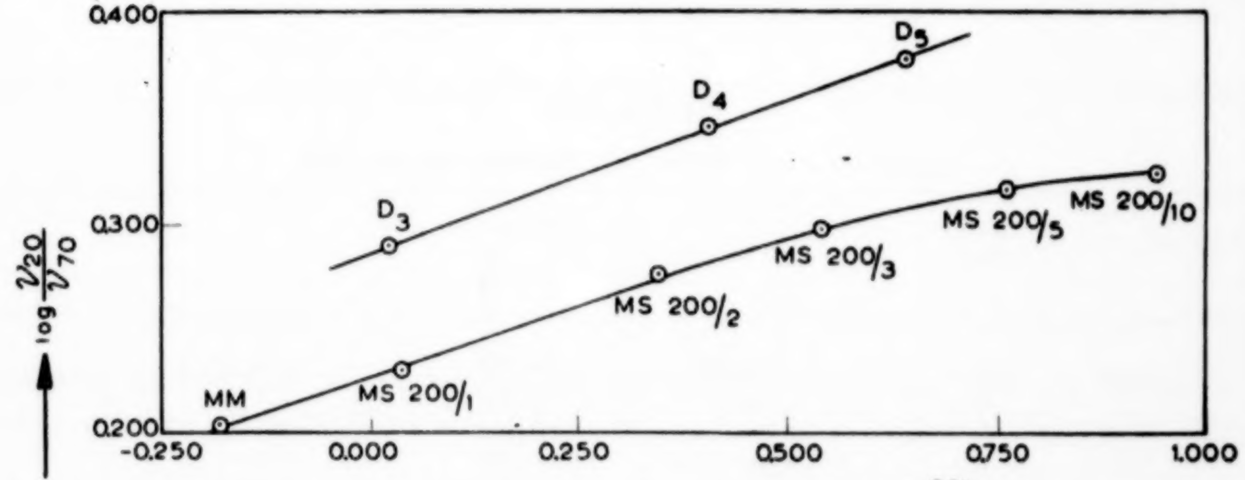


Fig. 77. F.V.T.I. of silicones plotted against their log ν_{20} values.

It can be seen from the figure that the F.V.T.I. of the chain polymers increases with increasing log ν_{20} value until it reaches the limiting value 0.380 for higher log ν_{20} values. The F.V.T.I. values of the cyclic polymers are invariably higher than the F.V.T.I. values of the chain polymers of the same viscosity value.

IV. ANALYSES IN THE FIELD OF FATTY OILS

1. INTRODUCTION

The fatty oil industry has not yet made the same progress in the chemical processing of its products as is the case in the petroleum industry. After the initial success attained in the development of the fat-hardening technique, this industry has remained stationary for many years. However, the chemical modification of fatty oils is of vital importance and the development of modern processes in the fatty oil industry will depend to a large extent on the basic knowledge of its raw materials and the fundamental study of possible chemical transformations.

The development of analytical methods is essential for the study of these processes. *Chemical* methods of analysis (BERTRAM's determination of saturated fatty acids[55], estimation of olefinic unsaturation by means of hydrogen value[56,1] and ozone addition[2]) have found widespread use. In addition *physical* analytical techniques (spectrochemical methods, chromatographic separations, etc.) have proved to be valuable for fatty oil analysis. In particular molecular distillation[57] must be mentioned, which has turned out to be of great value for the investigation of polymerized oils and for the industrial concentration of vitamins from animal oils. The cascade fractionating molecular still[58] permits an efficient separation of higher molecular fatty acid derivatives (Fig. 78).

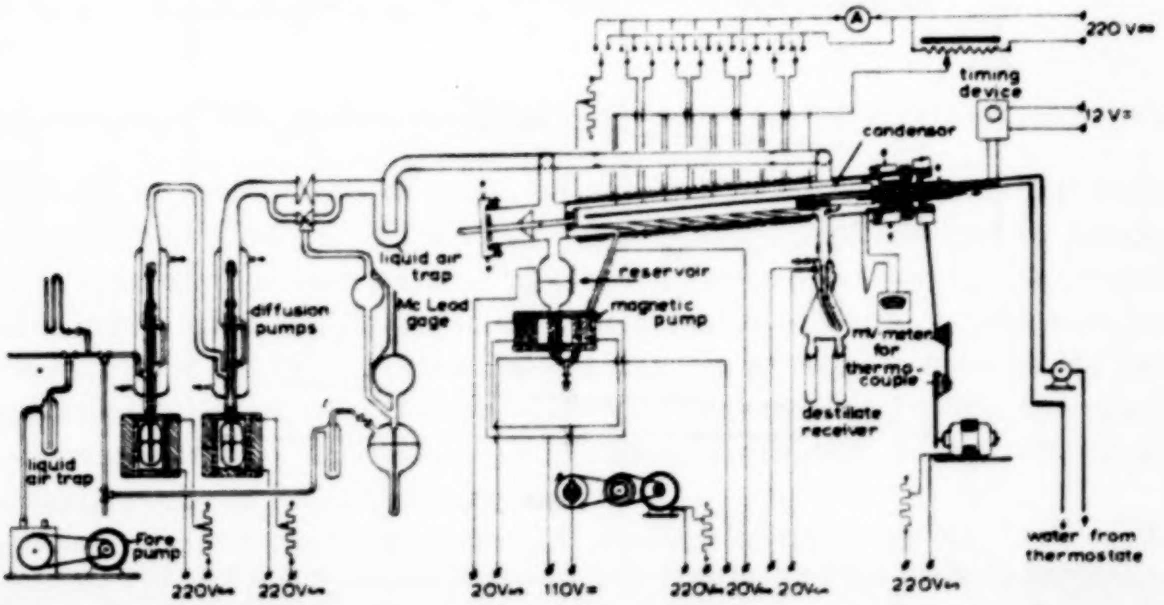

A
220 V~
timing device
12 V=
condensor
liquid air trap
reservoir
diffusion pumps
Mc Leod gage
magnetic pump
mV meter for thermo-couple
destillate receiver
liquid air trap
fore pump
water from thermostate
220V~
220V~
20V~
110V=
220V~
20V~
20V~
220V~

Fig. 78. Fractionating still with high separating power, according to BOOIJ.

On comparing the chemical composition of hydrocarbons and fatty oils, a certain parallelism between these two groups of products is found. Actually the difference is only due to the presence of a relatively small amount of oxygen in the esters. Thus, in principle, the structural analysis of fatty acid derivatives can be carried out by removing the oxygen and transforming the products into saturated hydrocarbons of corresponding structure. The proper methods of hydrocarbon analysis can then be applied to the hydrocarbon mixtures obtained. Several methods for deoxidation of fats have been recommended of which especially the direct high pressure hydrogenation and the Grignard method are mentioned here.

For the direct graphical representation of non-branched, non-conjugated and non-polymerized fatty oils, a general diagram has recently been constructed by TELS *et al.*[59]. In this diagram the specific refraction $r^{20}_{\text{spec.}}$ is plotted *vs.* the iodine value (*cf.* Fig. 79). Triglyceride mixtures containing per average molecule the same number of carbon atoms are represented by a set of parallels; the average number of double bonds follows from a bundle of curves converging to the limiting point of the graph, which point indicates the values of $r^{20}_{\text{spec.}}$ and the iodine value ($r^{20}_{\text{spec.}} = 0.3309$; iodine value $= 0$) when the molecular weight of the mixture approaches infinity.

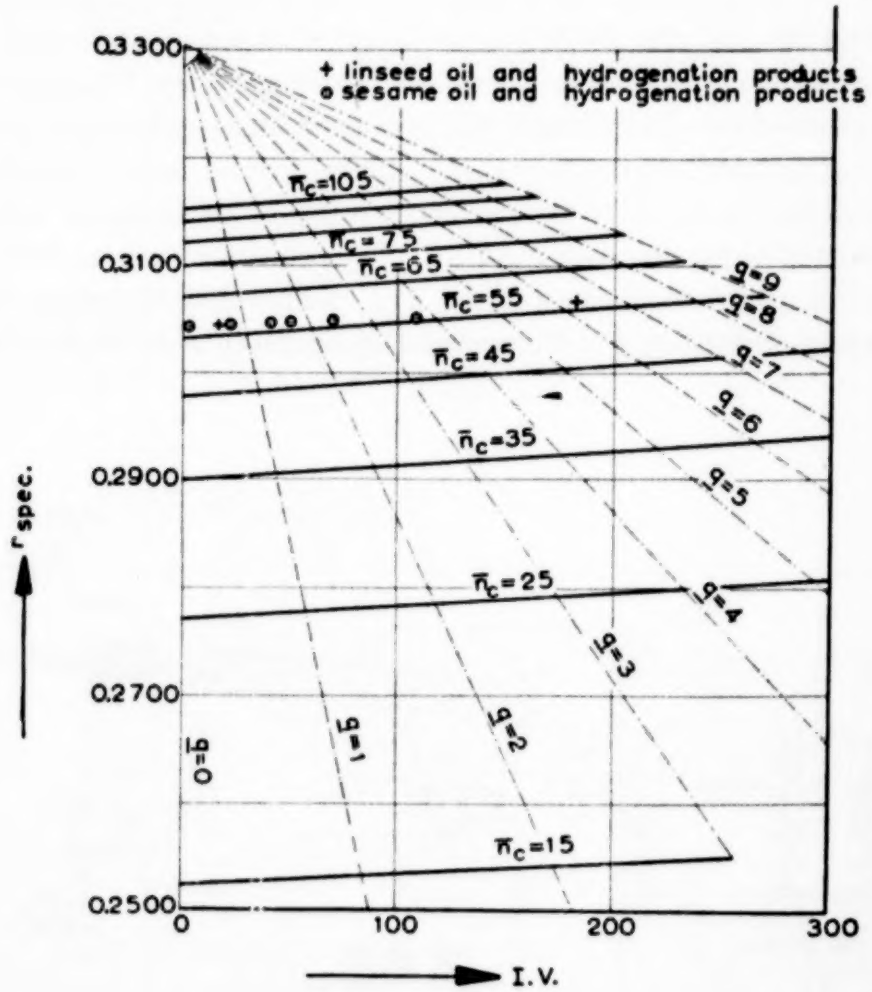


Fig. 79. General diagram for the representation of non-branched, non conjugated and non-polymerized fatty oils. $\bar{n}_c$ = number of carbon atoms per average triglyceride molecule; q = number of double bonds per average triglyceride molecule.

It should be remarked, that in several respects fatty oils and related products usually have a far less complicated character than have mineral oil products. The number of fatty acids occurring in natural fats is limited and certain structural elements, which contribute considerably to the composition of mineral oils (cyclic compounds, branchings) hardly occur. On the other hand, phenomena such as *cis-trans* isomerism, although certainly occurring in different cases in the field of mineral oils, play a more important part in fatty oil technology and have found valuable applications.

The chemical and physical properties of fatty oils depend largely on the nature of the fatty acids of which they are composed. This is reflected in the methods of classification of oils and fats, which methods are mainly based on two important structural characteristics:

(a) The degree of unsaturation, indicated, for example, by the *iodine value*, which gives the amount of iodine taken up, following standard methods. VAN DER STEUR[60] showed that the addition of halogen is an equilibrium reaction. The equilibrium constant depends on the nature and position of the double bond; yet in the majority of oils the various methods of iodine addition usually employed give values that vary little amongst themselves. In the fat-hardening industry especially, the iodine value is an important means of following the course of the reaction. When conjugated double bonds are present the normal addition of halogen fails; in these cases determination of the *hydrogen value* by quantitative hydrogenation with platinum- or palladium-catalysts[56,1], or quantitative ozonization[2] are to be preferred.

(b) The mean average molecular weight, for which the *saponification value* can be taken as a measure.

Several physical constants (density, refractive index, melting point) are closely related to the structural properties of fatty oils and are therefore used, not only for their classification, but also for following their chemical transformations (hydrogenation, polymerization, isomerization[61]). A more detailed study of these correlations will be of great help in obtaining more fundamental knowledge of the fatty oils and in developing new technical applications. The experiences and results obtained in the field of mineral oils may be very useful in this respect.

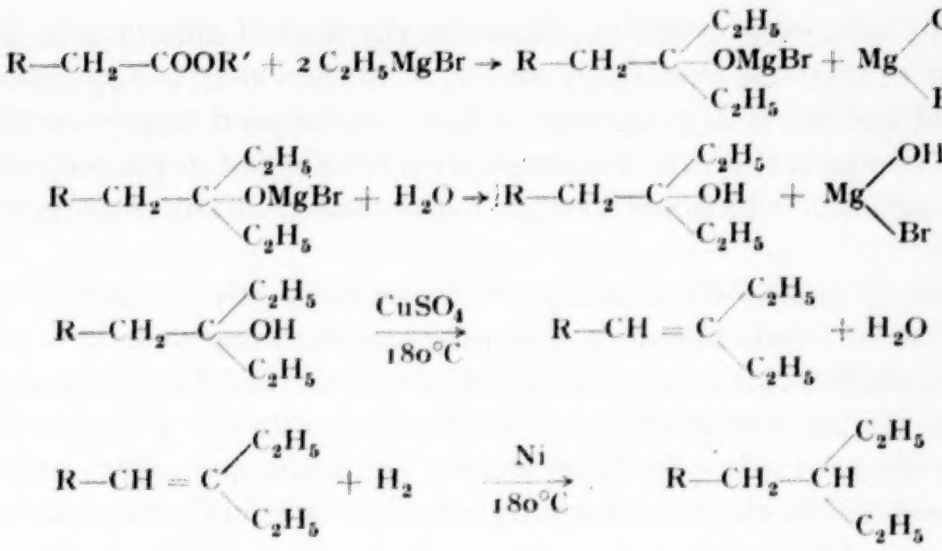
2. TRANSFORMATION OF FATTY ACID ESTERS INTO SATURATED HYDROCARBON MIXTURES

For the structural analysis of cyclic fatty acid derivatives (polymerized drying oils, copolymerization products of fatty oils with various hydrocarbons), in principle the same graphical methods can be developed as have been described for the investigation of hydrocarbon mixtures. However, the construction of useful graphical representations is hampered by the fact that reliable data on physical constants are restricted to the normal saturated fatty acids and their methyl and ethyl esters; the synthesis of pure unsaturated fatty acids is already extremely difficult, to say nothing of more complicated cyclic or branched compounds.

Therefore in many cases the structural analysis of fatty oils has been carried out by expelling the oxygen and transforming the fatty acid esters into saturated hydrocarbons of corresponding structure. The proper graphical analytical methods can then be applied to these products. This deoxidation can be performed either by a high pressure hydrogenation[62] (330–350°C, 200 atm., 30% of a nickel-copper on kieselguhr catalyst)

$$R{-}CH_2{-}COOR' + H_2 \xrightarrow[330-350^\circ C]{NiCu} RCH_3 + CO_2 + R'H$$

or by a Grignard operation[63] with alkyl magnesium halide, dehydration of the resulting tertiary alcohols and saturation of the olefinic double bonds, *e.g.*:



The direct hydrogenation to deoxidize fatty acid esters results in hydrocarbons with one carbon atom less than the number present in the hydrocarbon chain of the original ester. The reaction can be carried out quantitatively, but it is a relatively drastic chemical operation. In the Grignard method the hydrocarbon chain of the molecule is lengthened; the reactions are executed at relatively low temperatures; the overall yield amounts to 70–90% of the theory.

These procedures are especially useful for the investigation of polymerization phenomena of drying oils. The formation of rings during the thermal polymerization of linseed oil and tung oil, evidence for KAPPELMEIER's theory[65] of the diene type condensation reaction of drying oils at elevated temperatures, was confirmed by means of these methods[63,64]. Fig. 80 shows that thermal polymerization of linseed oil and

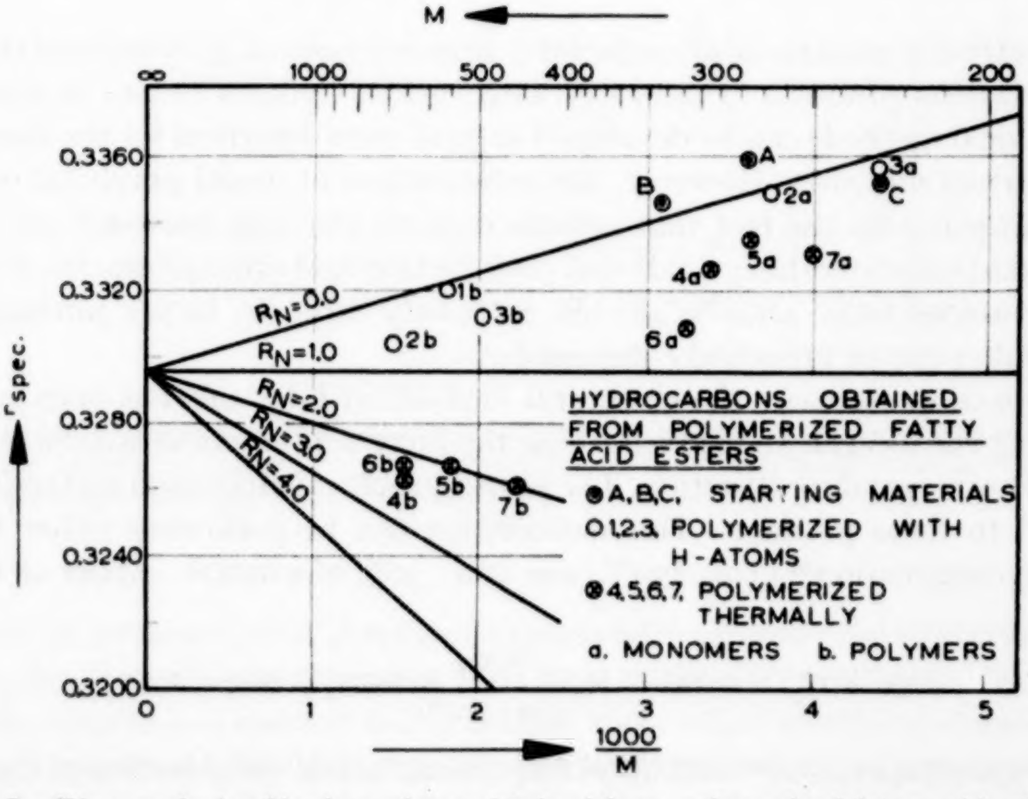
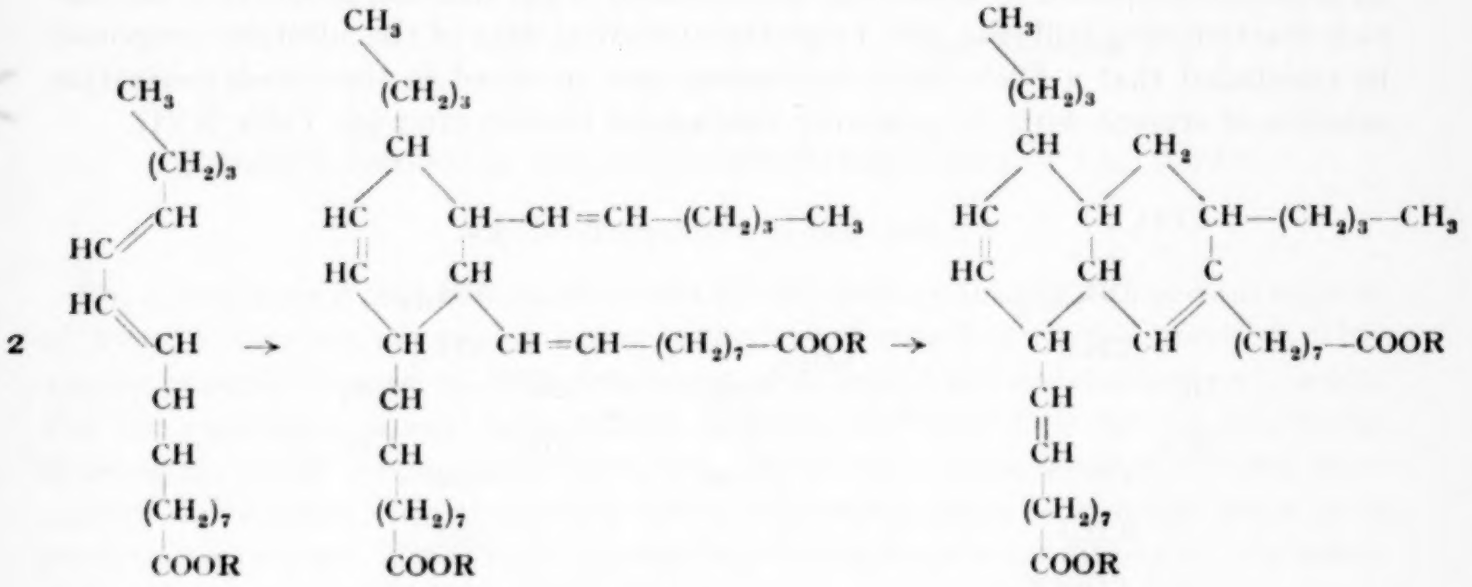


Fig. 80. Ring analysis of hydrocarbons obtained from polymerized fatty acid esters.

tung oil fatty acid esters leads chiefly to formation of dimers, containing approximately two rings per molecule; some cyclization of the esters also occurs. A possible reaction scheme can be represented as follows



elaeostearic acid ester

Diels-Alder adduct

bicyclic dimer

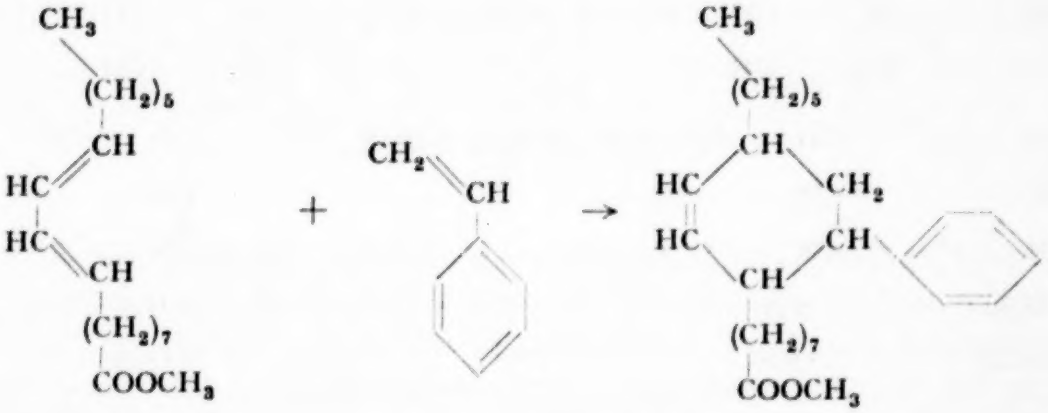
TABLE XVI

ANALYSIS OF COPOLYMERIZATION-PRODUCT OF STYRENE WITH METHYL LINOLEATE

	Properties of addition compound		*Properties of saturated hydrocarbon obtained from the addition compound by the Grignard method*	
	observed	*theoretical for Diels-Alder adduct*	*observed*	*calculated for $C_{28}H_{54}$*
n_D^{20}	1.5067	—	1.4768	—
d_4^{20}	0.9631	—	0.8668	—
$r_{spec.}^{20}$	0.3088	0.3067 (Eisenlohr) 0.3084 (Vogel)	0.3257	0.3253
Mol. wt.	403	398.6	395	390.7
Saponif. value	140.0	140.7	—	—
Iodine value (Wijs)	64.8	63.7	—	—
%C	81.27	81.35	86.11	86.07
%H	10.49	10.62	13.94	13.93
Average number of rings per molecule: from %H and mol. wt.			1.99	2.00
from *n*, *d* and mol. wt.			2.07	2.00

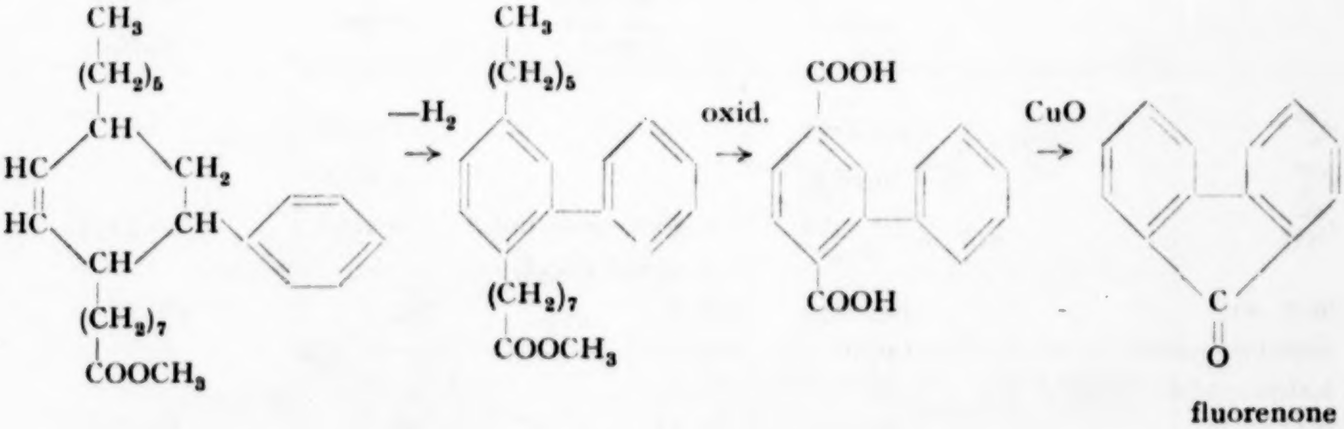
In the low temperature polymerization of these esters by the action of hydrogen atoms at room temperature cyclization is, on the contrary, of little importance[66]. Thus the application of the ring-analysis method to hydrocarbon mixtures obtained from polymerized esters by deoxidation, allows one to compare the structure of polymerization products obtained under different conditions.

Sie[67] allowed methyl linoleate to react with gaseous styrene at 280°C and isolated an addition compound by molecular fractionation of the reaction products in the cascade fractionating still (Fig. 78). From the analytical data of the addition compound he concluded that a Diels-Alder mechanism was involved in the copolymerization reaction of styrene with the primarily conjugated linoleic ester (*cf.* Table XVI):

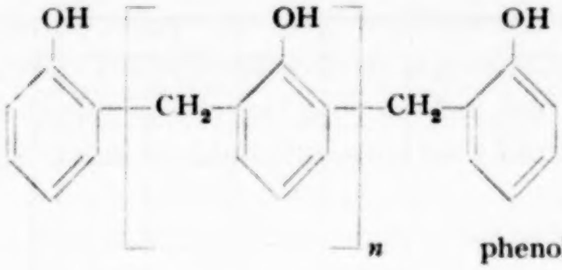


In order to establish the structure of the addition compound it was converted into the corresponding saturated hydrocarbon $C_{28}H_{54}$ by means of the above-mentioned Grignard reaction with methyl magnesium iodide; in this way the bicyclic character of the compound was proved (*cf.* Table XVI).

The structure was confirmed further by the following degradation reactions of the adduct[67]:


fluorenone

Another example of the use of deoxidation of oxygen-containing compounds for their structural analysis was given by Wijnands *et al.*[68], who investigated the structure of novolaks, prepared by polycondensation of formaldehyde with phenol, *p*-cresol and *m*-cresol. The novolaks were transformed into saturated hydrocarbon mixtures by direct hydrogenation. Ultimate analysis of the hydrocarbons confirmed the linear structure of the novolaks:



phenol-novolak

3. DIRECT GRAPHICAL TRACING OF TRANSFORMATIONS OF FATTY OILS

a. Hydrogenation of fatty oils

For a long time it was impossible to obtain satisfactory insight into several aspects of the fat hydrogenation process owing to the lack of reliable analytical methods. This was for example the case with the separation of saturated and unsaturated fatty acids. For this separation several inconvenient methods were used that did not favour the drawing of reliable conclusions from hydrogenation data, although they enabled WILLIAMS[69] to represent the theoretical limits of possible ways of hydrogenation in a general diagram and to study the influence of hydrogenation conditions on the selectivity of the process more closely.

An accurate investigation of these problems was, however, only possible after the development of reliable methods of analysis. Particularly BERTRAM's method[55] for the determination of saturated fatty acids should be mentioned. VAN VLODROP[70] proved its usefulness for the study of the hydrogenation of several fatty acid esters (oleic, linoleic, elaeostearic).

The importance of the hydrogenation of fatty oils lies chiefly in the fact that the melting point rises owing to partial saturation of the double bonds of the unsaturated fatty acid groups present in the glycerides. For practical reasons, especially in the case of the margarine industry, it is very important that the starting material, consisting for the greater part of mixed glycerides of mono-, di- and possibly tri-unsaturated fatty acids, should be hydrogenated in such a way that a product is obtained with a homogeneous consistency. This is possible by using a *selective* hydrogenation process, in which the poly-unsaturated fatty acids (linolenic, linoleic) are transformed into mono-unsaturated ones, while the percentage of saturated acids remains constant; a good selectivity is also desirable in connection with the stability of the product. Although side reactions influence the properties of the end-product (particularly *cis-trans* isomerism of mono-unsaturates is accompanied by a considerable increase in the melting point), the diagram of WILLIAMS appears to be a valuable representation of selectivity problems of the fat hydrogenation process.

In Fig. 81 the course of the hydrogenation of linoleic acid esters at various temperatures, pressures, quantities of catalyst and contact conditions, is represented. This figure gives a clear picture of the influence of reaction conditions on the selectivity of the process: higher temperatures and low hydrogen pressures promote the selectivity of the hydrogenation. The particular importance of the diagram is, that it shows under which conditions any desired point of the diagram — that is to say any desired composition of esters — may be obtained from the starting material. In Section VI the selective hydrogenation of linoleic esters is described in more detail, in connection with the characterization of hydrogenation catalysts (See p. 499).

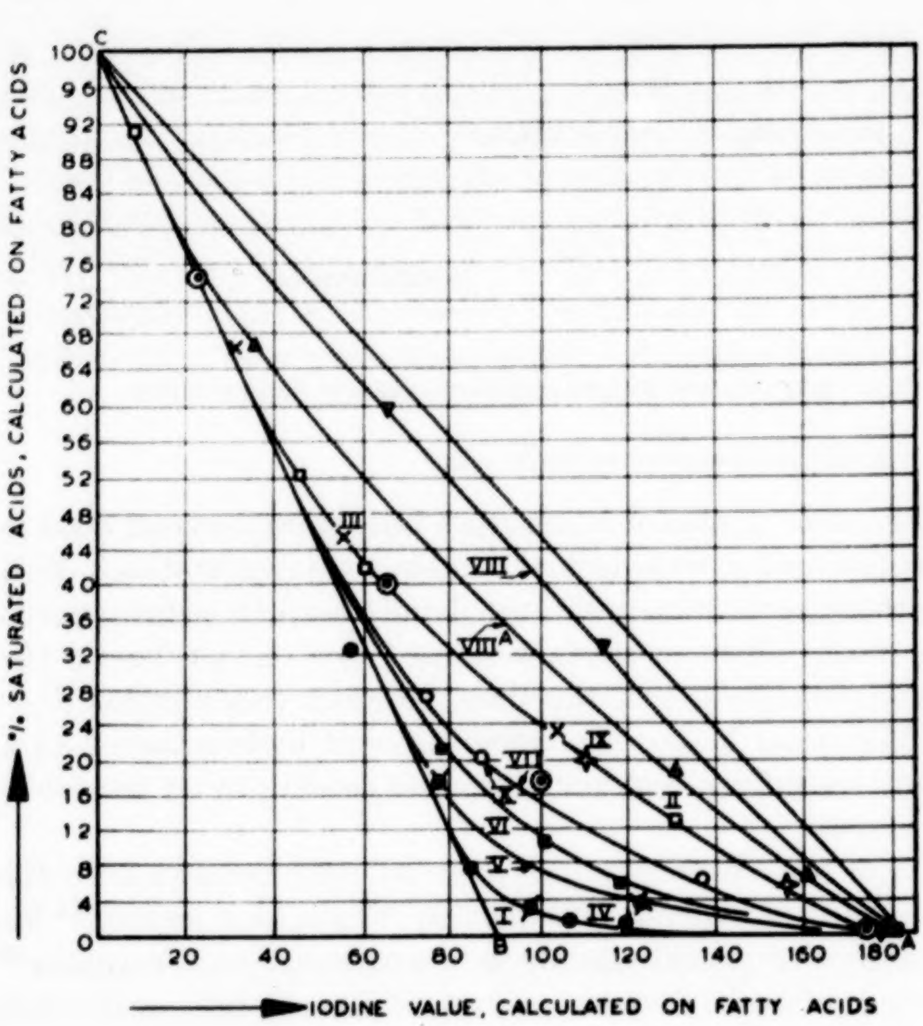


Fig. 81. Hydrogenation of linoleic esters.

× 3 % Ni-guhr, 50°C, 100 atm.
○ 2.5% Ni-guhr, 90°C, 1 atm.
● ⌀ 2 % Ni-guhr, 180°C, 1 atm.
◎ 2 % Ni-guhr, 180°C, 100 atm.
✖ 30 % Ni-guhr, 180°C, 1 atm.
▲ 10 % Pt-carbon, 20°C, 100 atm.
✧ 10 % Pt-carbon, 30°C, 0.1 atm.
□ 10 % Pt-carbon, 30°C, 1 atm.
▼ 10 % Pt-carbon, 50–65°C, 100 atm.
■ 10 % Pt-carbon, 180°C 1 atm.

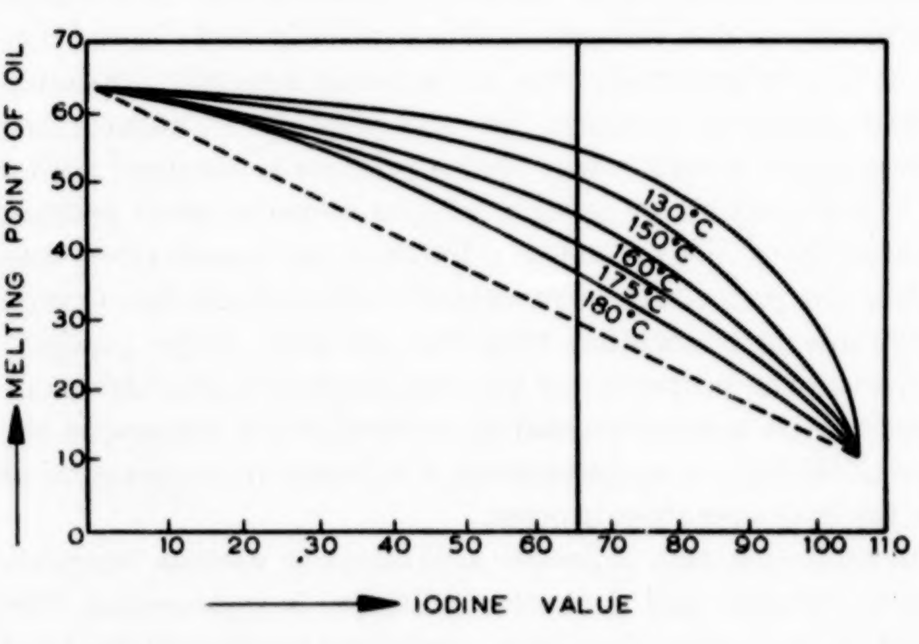


Fig. 82. Melting points and iodine values of cottonseed oil, hydrogenated at different temperatures, according to Williams[69].

It will be clear that the change in the melting point is closely connected with the conditions under which the hydrogenation process has been carried out. Not only the amount of solid saturated fatty acids, but also the amount of solid unsaturates formed during the process by isomerization, influences the melting point of the reaction product; hence no definite relationship can be given between iodine value and melting point (*cf.* Fig. 82). In practice, the refractive index is generally used besides the melting point for a rapid control of the saturation process, because the relationship between refractive index and iodine value is about the same for a large number of oils (Fig. 83).

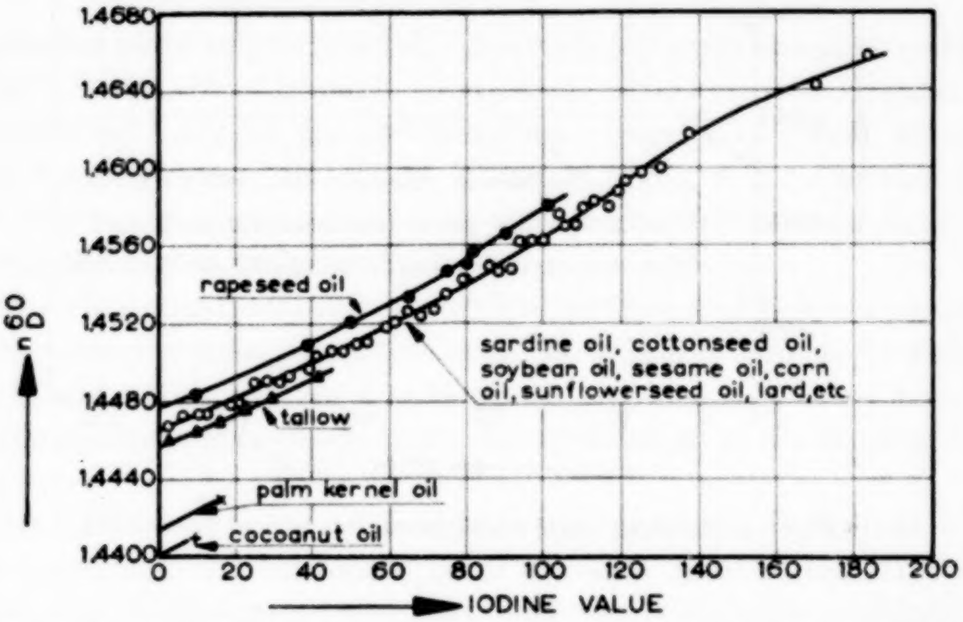


Fig. 83. Iodine value *vs.* refractive index for various hydrogenated oils, according to Bailey[71].

b. Polymerization of drying oils

According to Kappelmeier[65] the thermal polymerization of non-conjugated oils (linseed, perilla) takes place by a primary conjugation of the linoleic and linolenic acid groups, followed by a Diels-Alder type condensation reaction of the conjugated fatty acid groups (*cf.* p. 485). For the conjugation of the molecules a relatively high reaction temperature is necessary (approx. 300°C), unless proper conjugation catalysts are present; this explains the fact that thermal polymerization of conjugated oils like tung oil or catalytically conjugated linseed oil can be performed at much lower temperatures (200–250°C). Extensive research has shown that several active conjugation catalysts (sulphur dioxide, nickel, selenium) can be used as effective polymerization catalysts for non-conjugated drying oils, but do not influence the polymerization of conjugated oils to a large extent.

The action of sulphur dioxide in the conjugation (activation) of linseed oil and similar oils was studied by Van Vlodrop *et al.*[72]. In general relatively high pressures (100–150 atm.) are required to obtain a reasonable conjugation at lower temperatures (160–180°C). Later experiments[73] showed that linseed oil can also be activated at normal pressure by introducing gaseous SO_2 at 285–300°C; however, efficient precautions should be taken to avoid any influence of traces of oxygen which strongly promote polymerization of the activated oil at these high temperatures.

Graphical representation of the activation and polymerization phenomena of drying oils is possible by means of the specific refraction and the iodine value[74], as shown in Fig. 84.

In this diagram the triglycerides of pure linolenic, linoleic, oleic and stearic acid are represented by the points D, C, B and A, respectively; the values for the specific

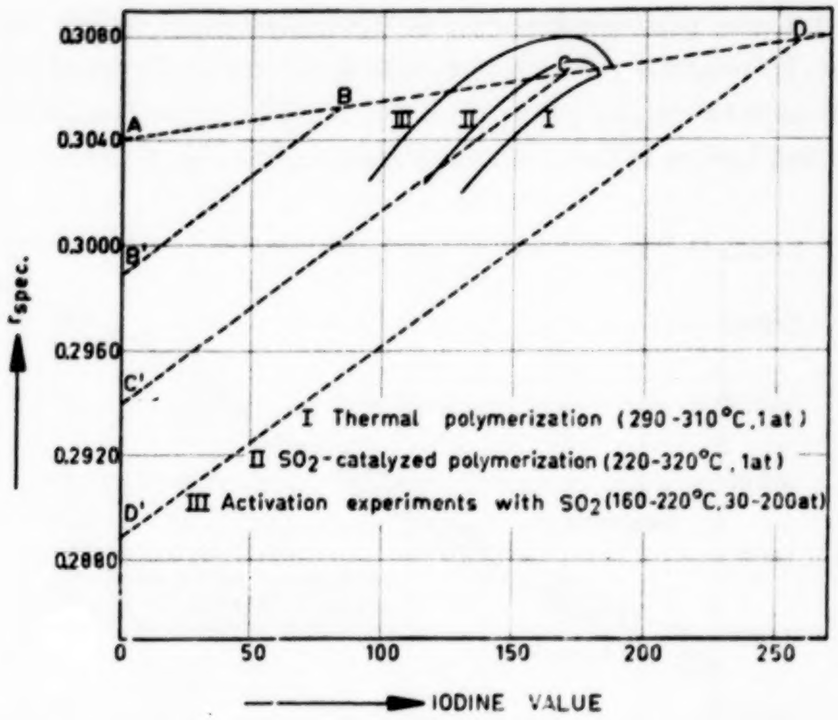


Fig. 84. Polymerization and isomerization of linseed oil.

refractions were calculated according to an equation recently given by Tels *et al.*[59] for non-conjugated, non-branched and non-polymerized glycerides:

$$r^{20}_{\text{spec.}} = 0.3307 + 1.68 \cdot 10^{-5}\ \text{I.V.} - 1.41 \cdot 10^{-4}\ \text{S.V.} \quad . \ . \ . \ . \ . \ . \quad (80)$$

in which I.V. = the iodine value
S.V. = the saponification value.

Hydrogenation experiments with the triglycerides are given by the curve D-C-B-A; theoretical polymerization curves of the esters (assuming removal of the double bonds without any change in the elementary composition) can be represented by D-D', C-C' and B-B'.

Conjugation of double bonds is demonstrated by an increase in the specific refraction of the experimental material. The role of this reaction in the polymerization of drying oils is shown by curves I, II, and III of Fig. 84. Curve I represents the thermal polymerization of linseed oil at 300°C. Owing to the low conjugation velocity, an increase in the specific refraction can hardly be detected; the conjugated molecules polymerize immediately at this relatively high process temperature. Curve II gives the course of sulphur dioxide-catalysed polymerization reactions. A considerable formation of conjugated molecules can be observed, especially in the initial stage of the process. Some typical conjugation (activation) experiments are shown by curve III.

Although the diagram does not give a quantitative interpretation of the heat-bodying phenomena of linseed oil it allows an easy comparison of the conjugation and polymerization reactions under different conditions. Chemical and physical analytical methods for the determination of conjugated double bonds (diene value, ultraviolet absorption spectra) confirmed the conclusions about the conjugation phenomena.

It should be remembered that the iodine value gives no reliable information about the unsaturation of polymerized and conjugated oils[60,61]; the diagrams discussed above should therefore be treated with some reserve. The application of improved analytical methods (hydrogen value, ozone addition) will improve the graphical analysis of conjugation and polymerization phenomena in this respect.

c. Cis-trans isomerism of fatty oils

The hardening action of sulphur dioxide on several fatty oils was observed by WATERMAN *et al.*[75] and DAHMEN[75a]. Although, in principle, *cis-trans* isomerization is possible with any unsaturated fatty oil, the elaidinization process is of special interest for the non-drying and semi-drying oils, where it brings about a considerable increase in melting point due to the conversion of oleic acid (and other mono-unsaturated fatty acid) esters into the higher melting elaido-forms.

Several active elaidinization catalysts are known[76] of which selenium and sulphur dioxide certainly are the most attractive ones. With liquid sulphur dioxide optimum results are obtained under relatively mild conditions (110–115°C, 35 atm., 3 h); the low reaction temperature is favourable for the application of the hardened oils in the margarine industry.

The hardening effect of fatty oil isomerization processes is limited by the fact that *cis-trans* conversion of the double bond of mono-unsaturated fatty acids is an equilibrium reaction; in the case of oleic and elaidic acid esters the equilibrium mixture consists of 67% elaidic acid and 33% oleic acid; this equilibrium ratio is practically independent of the isomerization temperature[77].

The course of the elaidinization reaction can be followed graphically by means of the critical demixing temperature of the oil, using, for example, aniline as a solvent. According to DAHMEN the rise in the critical demixing temperature is approximately proportional to the degree of elaidinization (*cf.* Fig. 85).

In Fig. 85 the critical demixing temperature of isomerized olive is plotted against the percentage of elaidinized oil (calculated on the amount of elaidinic acid that can

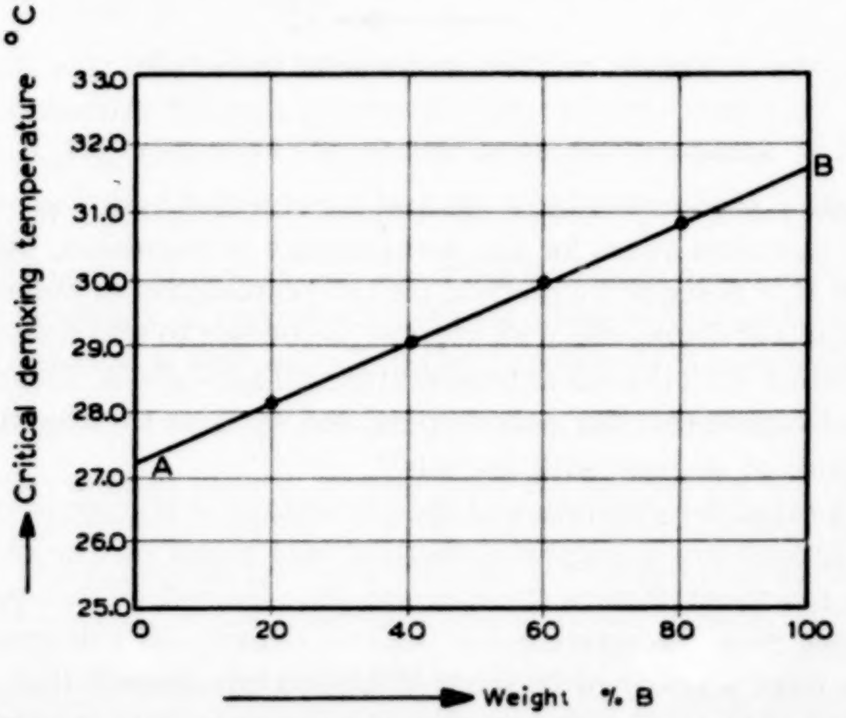


Fig. 85. Elaidinization of olive oil. Critical demixing temperatures (oil–aniline) plotted against composition of mixtures of refined olive oil A and a strongly elaidinized product B.

in practice be reached in the final product). Although this graphical method does not give the absolute percentage of elaidinic esters it allows a quick comparison of the *cis-trans* conversion under different conditions. The critical demixing temperature can be determined with good reproducibility and therefore should be preferred to melting point determinations.

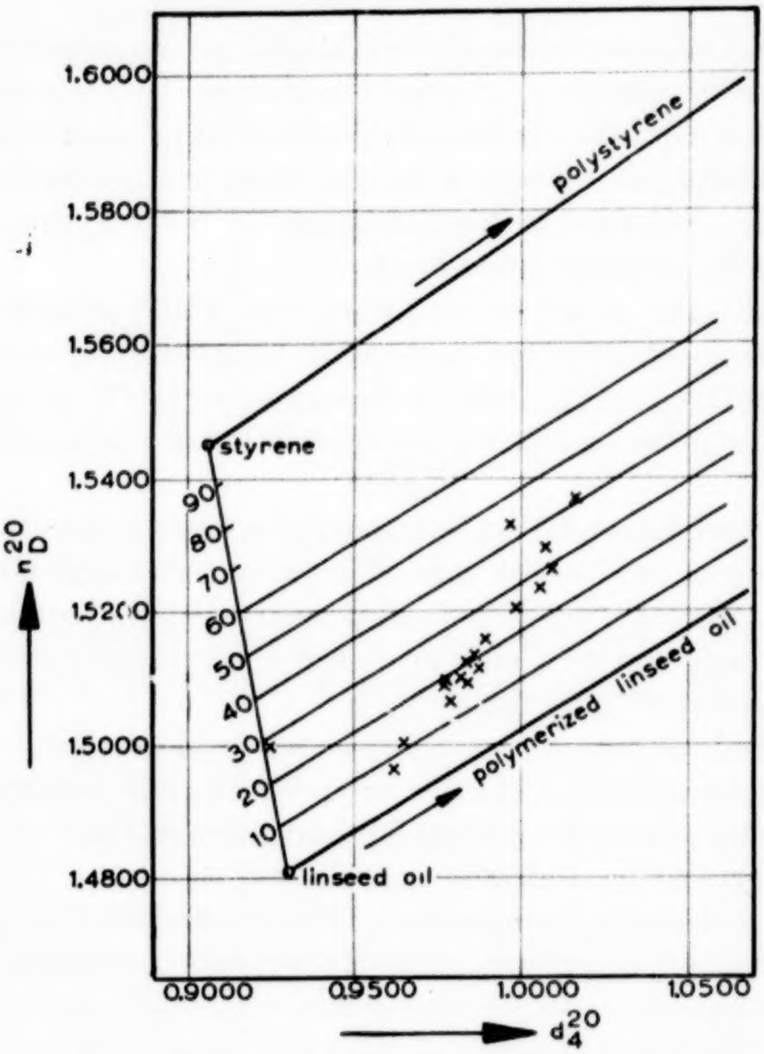


Fig. 86. Analysis of styrenated linseed oils.

4. GRAPHICAL ANALYSIS OF STYRENATED OILS

Copolymerization products of fatty oils and unsaturated hydrocarbons have become very important in recent years for the manufacture of varnishes, plasticizers, etc.

Waterman *et al.*[78] described a method for the preparation of homogeneous copolymerization products of drying oils with styrene, according to which styrene vapours are brought into contact with the oils at temperatures of 220–280°C. This method prevents the formation of high-molecular polystyrene and favours the chemical combination (copolymerization) of styrene with the oils[79].

To facilitate a rapid determination of the percentage of styrene in copolymerization products with linseed oil, a graphical method was based on the observation[80] that polymerization reactions of pure styrene and pure linseed oil can be represented by two parallel lines in a refractive index (n_D^{20}) *vs.* density (d_4^{20}) diagram (*cf.* Fig. 86).

Analysis of a large number of styrenated linseed oils showed that parallels, drawn between these two lines, indicate immediately the percentage of styrene in the products.

V. COMPOSITION OF COAL

Coal is mainly composed of carbon, hydrogen and oxygen and is formed from plants by a coalification process. During this process the oxygen, constituting about 40% of the plant material, is split off as, for example, H_2O and CO_2. The process can be represented by graphical tracing in a $\frac{H}{C}-\frac{O}{C}$ diagram, introduced by VAN KREVELEN[81,82] (Fig. 87). The $\frac{O}{C}$-scale is twice as large as the $\frac{H}{C}$-scale. Methane is on the $\frac{H}{C}$-axis at $\frac{H}{C} = 4$ (indicated by B), carbon is at the origin (indicated by D), carbon dioxide is on the $\frac{O}{C}$-axis at $\frac{O}{C} = 2$ (indicated by E) and water at infinity $\left(\frac{H}{C} = \infty; \frac{O}{C} = \infty\right)$ in the direction DA. The use of the diagram is not restricted to the triangle given, though this triangle covers most of the practical cases.

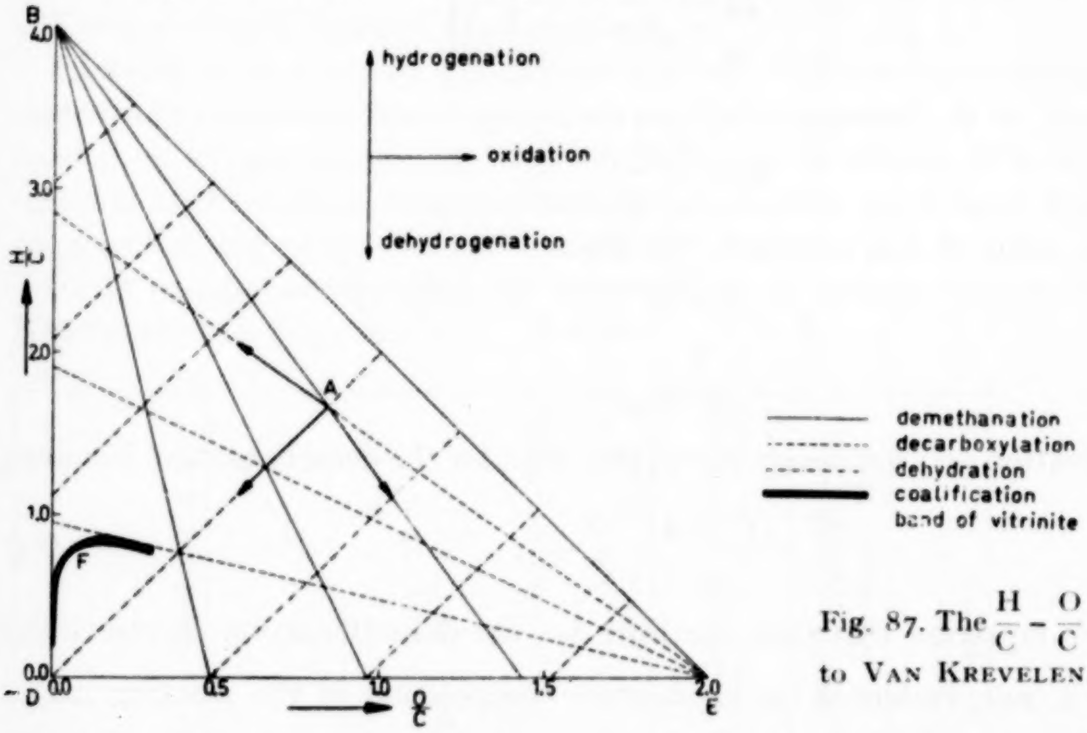


Fig. 87. The $\frac{H}{C}-\frac{O}{C}$ diagram according to VAN KREVELEN.

In this diagram any product composed of carbon, hydrogen and oxygen can be indicated if the molecular formula is known from ultimate analysis.

Pure cellulose $(C_6H_{10}O_5)_n$, for example, is indicated by point A in the diagram $\left(\frac{H}{C} = \frac{5}{3}; \frac{O}{C} = \frac{5}{6}\right)$. If methane ($CH_4$) or carbon dioxide ($CO_2$) or water ($H_2O$) are expelled from cellulose, the compositions of the resulting products move along straight lines, connecting point B with A, if methane is split off, along EA, if carbon dioxide is split off and along AD, if H_2O is split off, all in the direction of the indicated arrows.

In the $\frac{H}{C}-\frac{O}{C}$ diagram several sets of straight lines are constructed, one set for the demethanation (the various lines diverging from B), one set for the decarboxylation (the various lines diverging from E), and one for the dehydration, the various lines running parallel. The equations for these sets can be derived as follows, assuming the molecular formula CH_pO_q for the starting material (coal, lignine, cellulose).

1. DEMETHANATION

If d is the fraction of carbon atoms that is transformed into CH_4, then $4d$ hydrogen atoms are split off. The molecular formula for the resulting product is:

$$C_{1-d}H_{p-4d}O_q$$

If the set of straight lines for the demethanation is represented by the equation

$$\frac{H}{C} = a\,\frac{O}{C} + b \quad \ldots\ldots\ldots\ldots \quad (81)$$

then the following equation holds

$$p = a\,q + b \quad \ldots\ldots\ldots\ldots \quad (82)$$

and

$$\frac{p-4d}{1-d} = a\,\frac{q}{1-d} + b \quad \ldots\ldots\ldots\ldots \quad (83)$$

a and b can be solved from these equations by first subtracting eqn. (83) from eqn. (82)

$$p - \frac{p-4d}{1-d} = a\left(q - \frac{q}{1-d}\right)$$

or

$$a = \frac{p-4}{q}$$

Substituting this value of a in equation (82) gives

$$p = \frac{p-4}{q}\cdot q + b$$

$$b = 4$$

Consequently equation (81) for the set of straight lines for the demethanation becomes

$$\frac{H}{C} = \frac{p-4}{q}\cdot\frac{O}{C} + 4 \quad \ldots\ldots\ldots\ldots \quad (84)$$

It follows from equation (84) that the lines for the demethanation intersect the $\frac{H}{C}$-axis in $\frac{H}{C} = 4$, independent of the elementary composition of the starting material. Furthermore the tangent a of the slope of the lines is equal to $\frac{p-4}{q}$ and consequently varies with the elementary composition of the starting material. These facts are shown in Fig. 87.

2. DEHYDRATION

The equation for the set of lines for the dehydration can be derived in the same way as has been discussed for the demethanation. The result is

$$\frac{H}{C} = 2\cdot\frac{O}{C} + (p-2q) \quad \ldots\ldots\ldots \quad (85)$$

It can be concluded from this equation that the tangent of the slope of the lines for the dehydration is constant and equal to 2. This means that the lines for the dehydration are parallel in the $\left[\frac{H}{C} - \frac{O}{C}\right]$-diagram; which is shown in Fig. 87. The lines intersect the $\frac{H}{C}$-axis in $\frac{H}{C} = (p-2q)$, the point of intersection being dependent on the elementary composition of the starting material.

3. DECARBOXYLATION

The following equation for the set of lines for the decarboxylation can be derived:

$$\frac{H}{C} = \frac{p}{q-2} \cdot \frac{O}{C} - \frac{2p}{q-2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; (86)$$

It follows from this equation that the tangent of the slope of the decarboxylation lines is dependent on the elementary composition of the starting material and is equal to $\frac{p}{q-2}$. All the lines intersect the $\frac{O}{C}$-axis in $\frac{O}{C} = 2$, which is shown in Fig. 87.

In Fig. 87 a coalification band F for vitrinites is also represented. From the straight lines in the $\frac{H}{C}$-$\frac{O}{C}$-diagram for the demethanation, the dehydration and the decarboxylation it follows that initially CO_2 is split off during the coalification process and that in the final stages mainly CH_4 is split off.

Recently it has proved possible to convert cellulose by catalytic hydrogenation under mild conditions into ring-containing hydrocarbons[83]. If we assume HAWORTH's concept of oxygen-containing rings in cellulose to be correct, it is certain that, on the removal of the oxygen, rings containing carbon only, are formed from products with rings containing oxygen as well as carbon.

For a discussion regarding the constitution of coal we refer to the book of VAN KREVELEN AND SCHUYER[82].

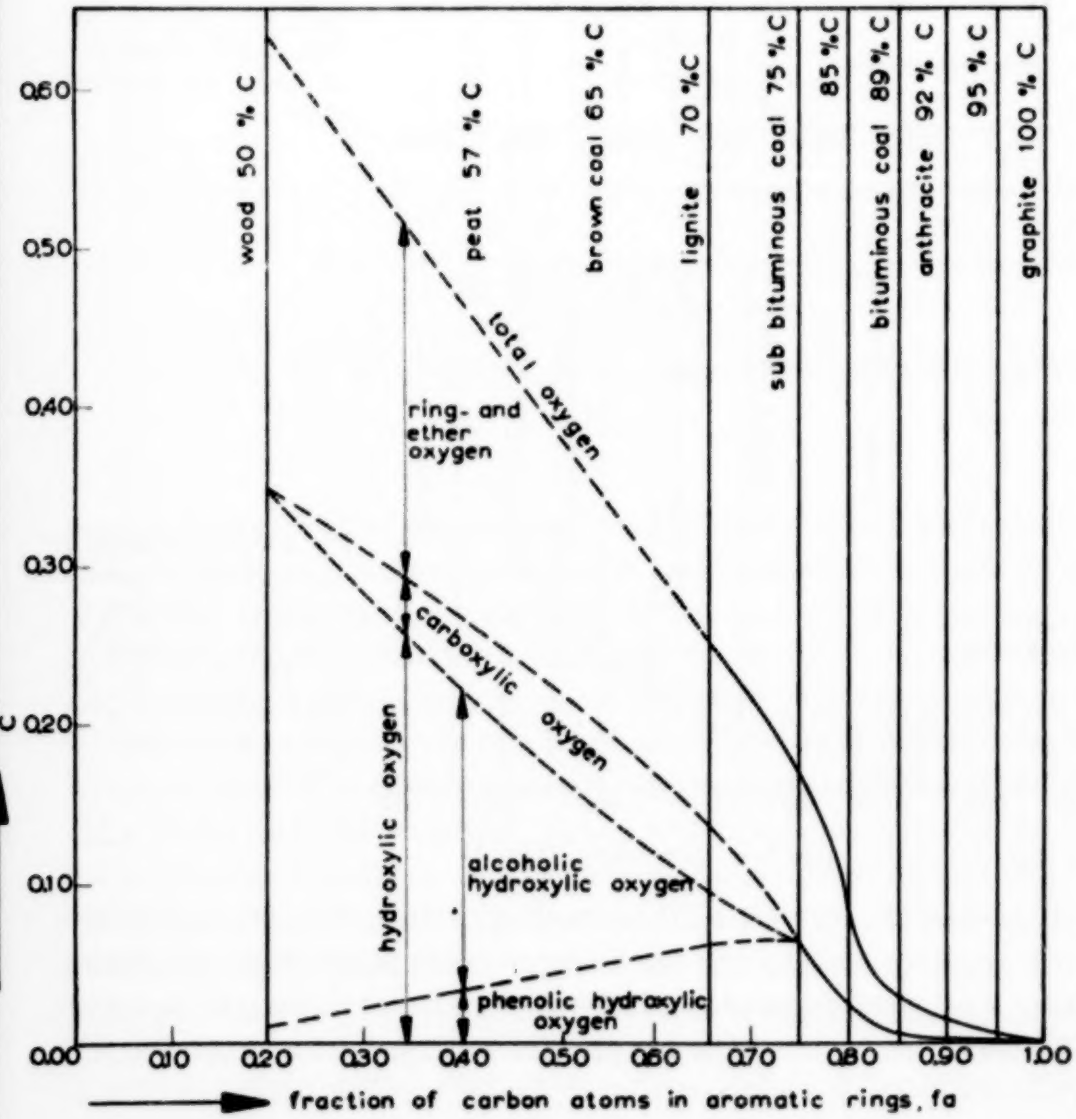


Fig. 88a. The conversion of the various oxygen-containing compounds during the coalification process, according to MEIJS.

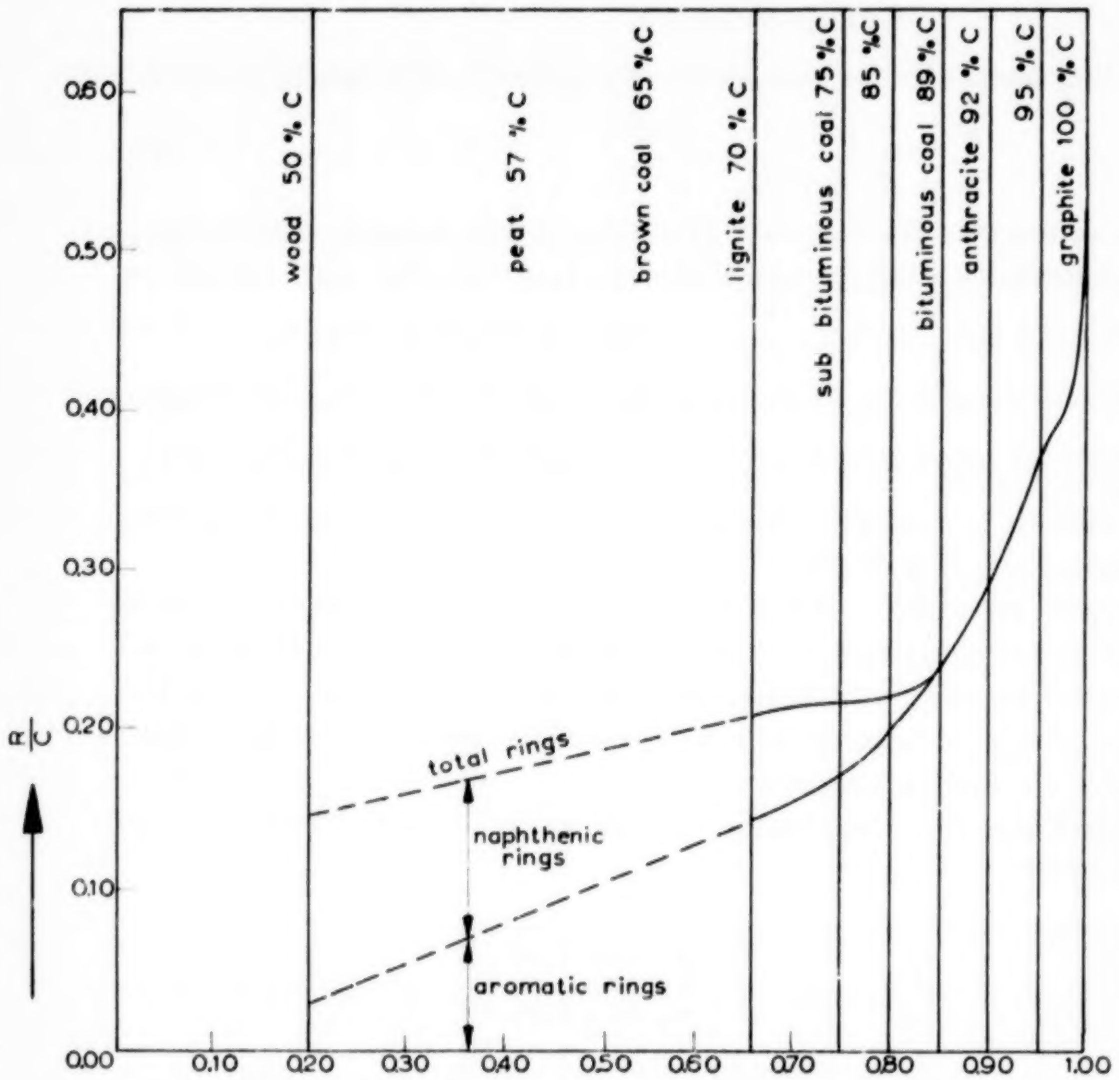


Fig. 88b. The change of naphthenic and aromatic rings during the coalification process, according to MEIJS. R/C = number of rings per carbon atom.

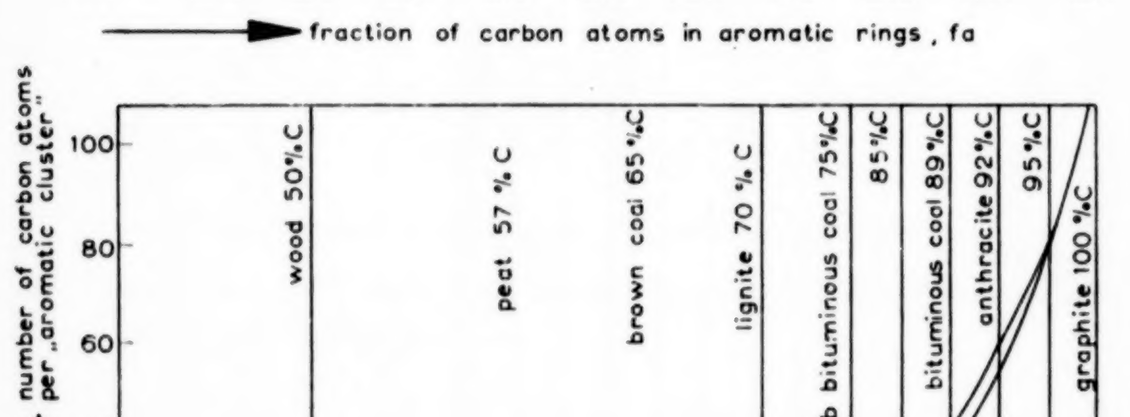


Fig. 88c. The change of the number of carbon atoms in naphthenic, aromatic and paraffinic structure during the coalification process, according to MEIJS.

Investigations of VAN KREVELEN and further studies of MEIJS[84] have led to the construction of various graphs, representing the changes in chemical structure during the coalification process, the conversion of the various oxygen-containing compounds and the formation of aromatic clusters. The graphs are represented in Figs. 88a, 88b and 88c.

VI. GRAPHICAL STATISTICAL METHODS FOR STUDYING CATALYTIC PROCESSES. CHARACTERIZATION OF CATALYSTS BY PARAMETERS

1. INTRODUCTION

Chemical reactions are generally connected with a change in chemical composition. A graphical representation of the reactions often facilitates a better understanding of the nature of the chemical transformations (Fig. 89). The change in various physical constants during the process can often be taken as an indication of the occurrence of changes in the chemical composition of the reactants (Figs. 1a and 1b).

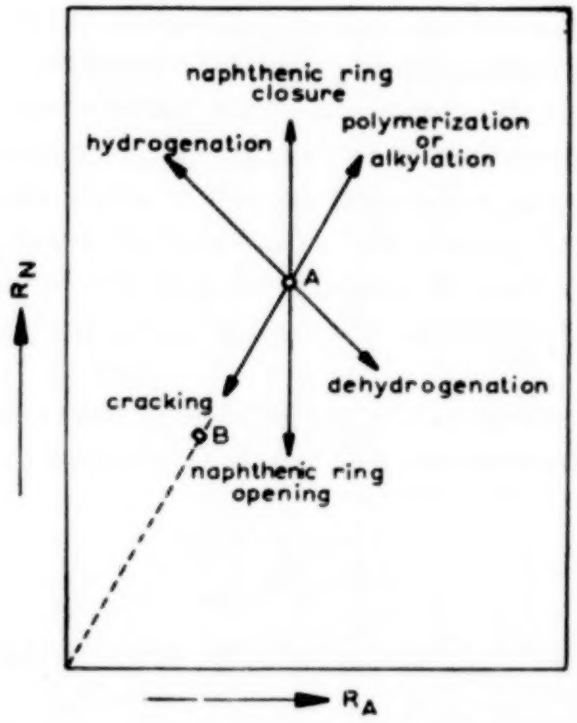


Fig. 89. Graphical tracing of reactions of hydrocarbon mixtures[85].

The use of physical constants is, however, limited in the case of more complicated chemical processes: the more complex the chemical change, the larger the number of physical properties necessary to investigate completely the chemical transformations. This especially holds when catalysts are involved in the reactions. When studying catalytic reactions we are dealing with catalysts as mixtures of a far more complicated nature than is the case, for example, in the structural analysis of hydrocarbon mixtures. The latter can be described, as was shown in the preceding sections, by means of a limited number of physical constants, from which either the chemical composition of the mixture or a series of other physical constants can easily be derived. For the characterization of catalysts completely different principles have to be applied even in simple cases, because in the case of a catalyst it is not chiefly its chemical composition that is important, but its chemical activity, which determines the result obtained by its chemical action.

In recent years the investigation of catalytic processes has led to better knowledge of the properties of catalysts and of the reaction kinetics. The complexity of the phenomena has, however, greatly hampered a real elucidation of the problems involved.

Recent work by WEBER[86,87] has shown that it is possible to determine the activity of catalysts from a completely practical point of view by correlating the more important actions of the catalyst as a function of the process variables (temperature, pressure, nature of catalyst) by means of simple equations, the validity of which has been proved for a large number of catalytic processes. These equations are especially useful in the study of simultaneous chemical reactions in which selectivity problems play a part. They are of great value for more systematical research on catalysts.

2. CHARACTERIZATION OF CATALYSTS

In the method of WEBER for the characterization of catalytical chemical reactions use is made of a very simple principle of *graphical tracing*, in which the most important actions of the catalyst, *viz. the conversion of the starting material, the formation of the desired products* and *the formation of by-products* are considered.

According to this principle a chemical process in which selectivity problems are involved, can be represented graphically as a *pseudo-ternary system*. The unconverted starting material (A), the desired product (B) and the byproducts (C) can be chosen as the "components" of this system; the course of the reactions can be plotted in a triangular diagram.

WEBER stated that *the change in concentration of the three components chosen, resulting from the variation of one reaction variable, can be represented by an equation of the second order*:

$$y = \frac{x\,(1 - x)}{a + bx} \quad \ldots\ldots\ldots\ldots\ldots \quad (87)$$

in which y and x represent the two co-ordinate lines of the diagram, while a and b are constants.

Equation (87) represents a *hyperbola* (Fig. 90); the equations of the asymptotes are

$$x = -\frac{a}{b}$$

$$bx + b^2y = a + b$$

It should be emphasized that only the part of the hyperbola within the triangle (Fig. 90) has practical significance.

If the starting material consists of two or more different substances, *e.g.*, A and A', the reaction products therefrom can still be regarded as three component systems, if unconverted A, unconverted A', and the combined products obtained from A and A', are represented as the three components. For these cases the following holds

$$y = x + \frac{x\,(1 - x)}{a + bx} \quad \ldots\ldots\ldots\ldots\ldots \quad (88)$$

in which y and x represent the retention of A and A', respectively, expressed as A/A_0 and A'/A_0' (in these ratios A and A' represent the concentrations of A and A', respectively, A_0 and A_0' being the concentrations of A and A' in the starting material), *cf.* Fig. 91.

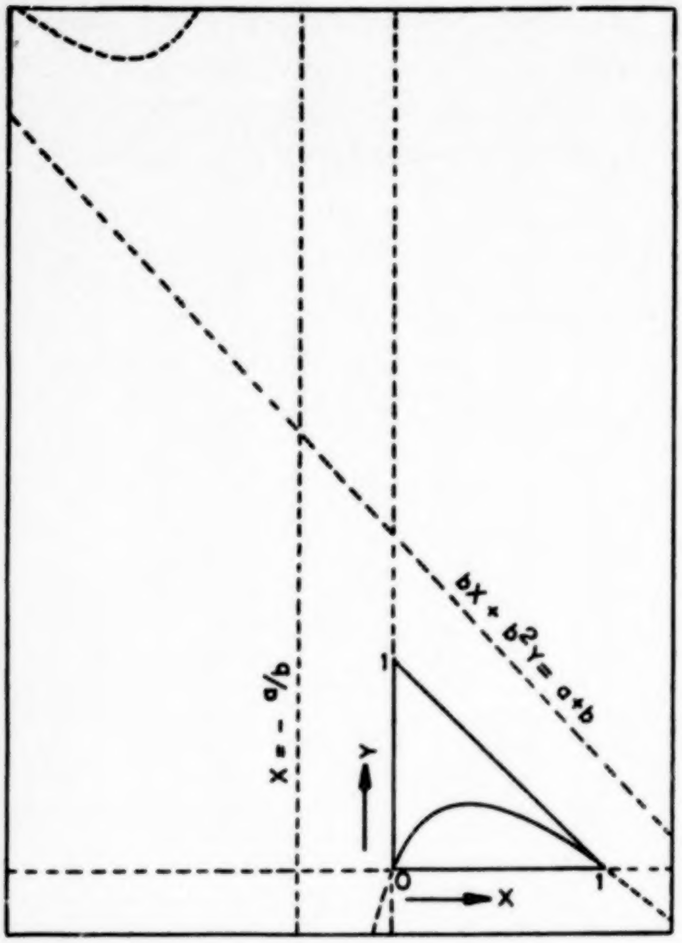


Fig. 90. Graphical representation of the hyperbola

$$y = \frac{x(1-x)}{a+bx} \qquad (a = 0.4,\ b = 0.9).$$

y = fraction of A transformed into B,
x = fraction of A transformed into C.

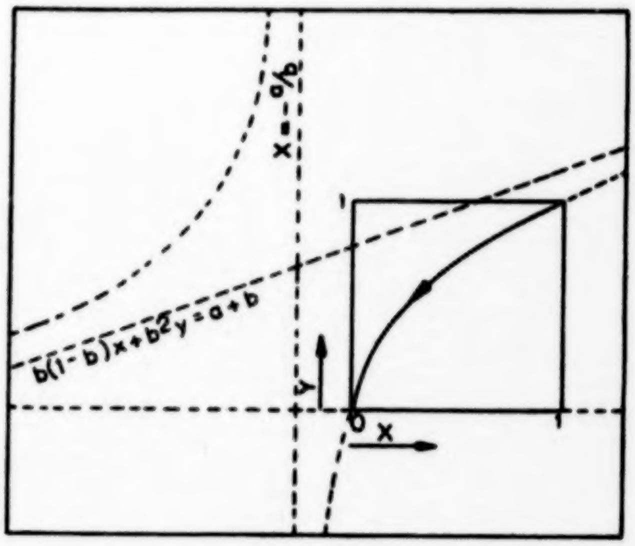


Fig. 91. Graphical representation of the hyperbola

$$y = x + \frac{x(1-x)}{a+bx} \qquad (a = 0.4,\ b = 1.6).$$

3. APPLICATIONS

The applicability of the hyperbolic equations will be demonstrated for the following processes (*cf.* Figs. 92–98).

a. Catalytic hydrogenation of linoleic esters[70,88]

This reaction is an example of a consecutive first order reaction[88]:

$$\text{linoleic ester} \xrightarrow{k_1} \text{oleic ester} \xrightarrow{k_2} \text{stearic ester}$$

Series of experiments carried out at a relatively high temperature (180°C) and at relatively low temperatures (20–90°C) with different catalysts and at different hydrogen pressures are represented in the triangular diagrams of Figs. 92 and 93, respectively. The course of each experiment can be represented by a hyperbola in accordance with equation (87); the values of *a* and *b* for the different experiments are collected in Table XVII.

TABLE XVII

CATALYTIC HYDROGENATION OF LINOLEIC ESTERS

REACTION COURSES ACCORDING TO THE HYPERBOLIC FORMULA

$$y = \frac{x(1 - x)}{a + bx}$$

	Reaction conditions			*a*	*b*
	2% Ni-guhr,	180°C,	1 atm.	0.0065	0.947
High temperature	30% Ni-guhr,	180°C,	1 atm.	0.0272	0.886
hydrogenations	10% Pt-carbon,	180°C,	1 atm.	0.0481	0.878
(*cf.* Fig. 92)	2% Ni-guhr,	180°C,	100 atm.	0.0950	0.978
Low temperature	2.5% Ni-guhr,	90°C,	1 atm.	0.117	0.712
hydrogenations	10% Pt-carbon,	30°C,	1 atm.	0.340	0.398
(*cf.* Fig. 93)	3% Ni-guhr,	50°C,	100 atm.	0.340	0.398
	10% Pt-carbon,	30°C,	0.1 atm.	0.340	0.398
	10% Pt-carbon,	20°C,	100 atm.	0.747	0.128
	10% Pt-carbon,	50–65°C,	100 atm.	1.660	2.210

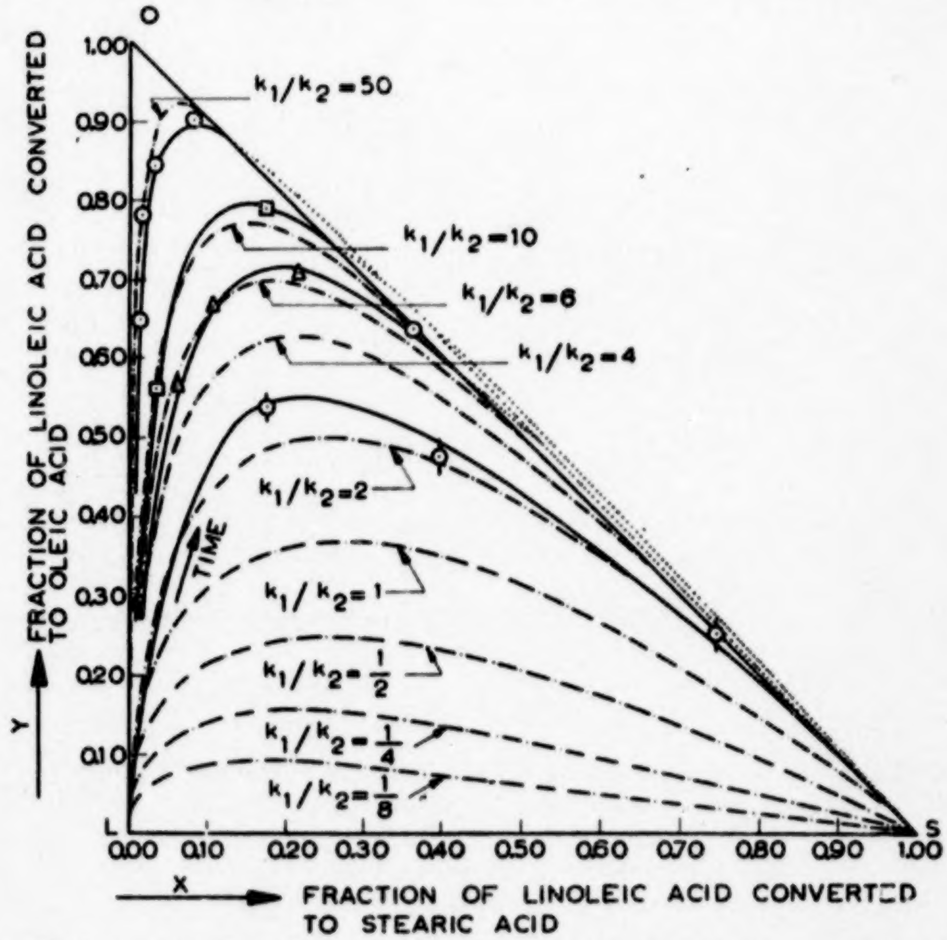


Fig. 92. Hydrogenation of linoleic esters at a relatively high temperature (180°C).

⊙	2% Ni-guhr,	180°C,	1 atm.
⊡	30% Ni-guhr,	180°C,	1 atm.
▲	10% Pt-carbon,	180°C,	1 atm.
⌽	2% Ni-guhr,	180°C,	100 atm.

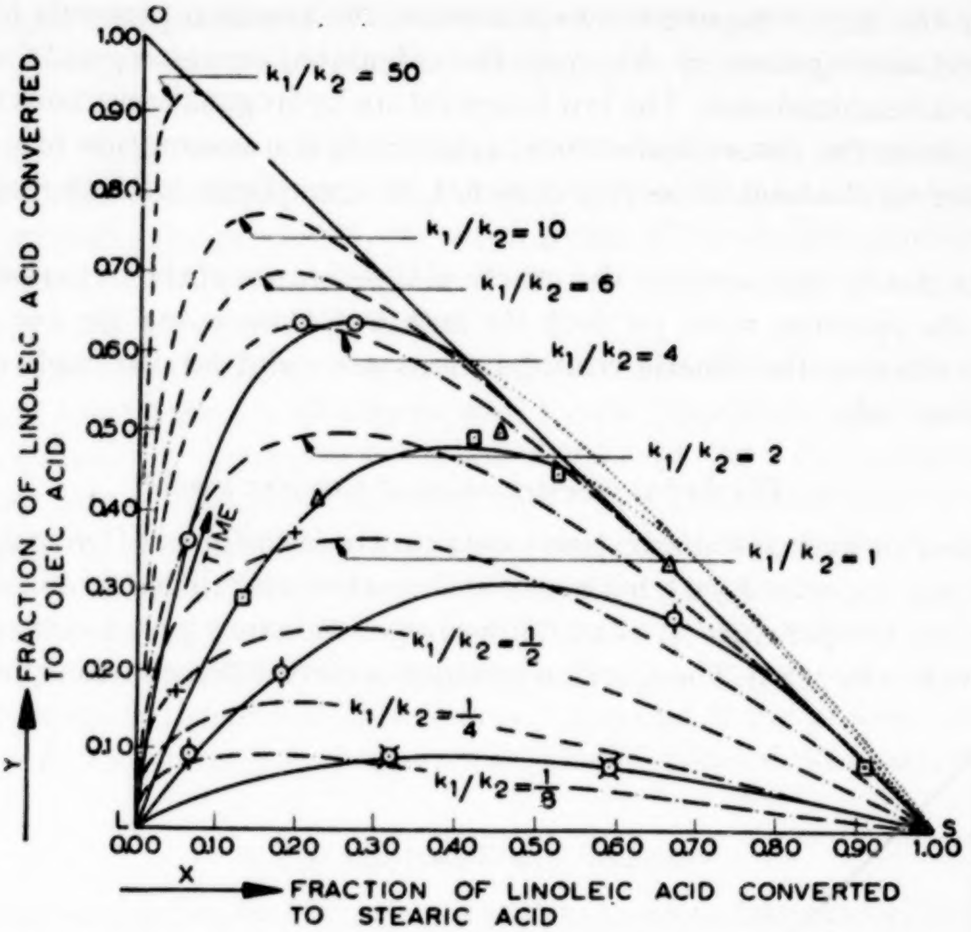


Fig. 93. Hydrogenation of linoleic esters at relatively low temperatures (20–90°C).

●	2.5% Ni-guhr,	90°C,	1 atm.
▣	10% Pt-carbon,	30°C,	1 atm.
▲	3% Ni-guhr,	50°C,	100 atm.
+	10% Pt-carbon,	30°C,	0.1 atm.
ϕ	10% Pt-carbon,	20°C,	100 atm.
✖	10% Pt-carbon,	50–65°C,	100 atm.

The catalytic hydrogenation of linoleic esters has also been treated kinetically by BOELHOUWER *et al.*[88]. If the velocity constants of the consecutive reactions are represented by k_1 and k_2 and first order kinetics are assumed, the following equations hold:

$$-\frac{\mathrm{d}L}{\mathrm{d}t} = k_1 L$$

$$\frac{\mathrm{d}O}{\mathrm{d}t} = k_1 L - k_2 O$$

$$\frac{\mathrm{d}S}{\mathrm{d}t} = k_2 O$$

in which L, O and S represent the molar concentrations of linoleic, oleic and stearic esters, respectively. With the aid of these equations it is possible to calculate the course of hydrogenation reactions for distinct constant values of the ratio r

$$r = \frac{k_1}{k_2}$$

and to represent them also in the triangular diagrams of Figs. 92 and 93. It is remarkable that for the high temperature experiments the reaction proceeds according to the theoretical assumptions (*cf.* Fig. 92): the calculated curves coincide with the experimentally determined ones. The low temperature hydrogenations, however, deviate considerably from the theoretical curves: apparently the assumption of a simple first order reaction mechanism is in this case not in accordance with the experimental results.

These data clearly demonstrate the practical significance of the hyperbolic equation of WEBER: *the equation holds for both the high temperature and the low temperature experiments,* whereas the kinetic considerations are valid for the high temperature hydrogenations only.

b. The hydro-isomerization of paraffin wax[89]

In a number of hydro-isomerization experiments paraffin wax (average molecular weight 375) was vaporized with hydrogen and treated with different catalysts (W.H.-S.V. 0.89–1.04, temperature 410–450°C, hydrogen pressure 32–102 atm., molar ratio hydrogen : wax = 61 : 183). The reaction products were distilled at atmospheric pressure

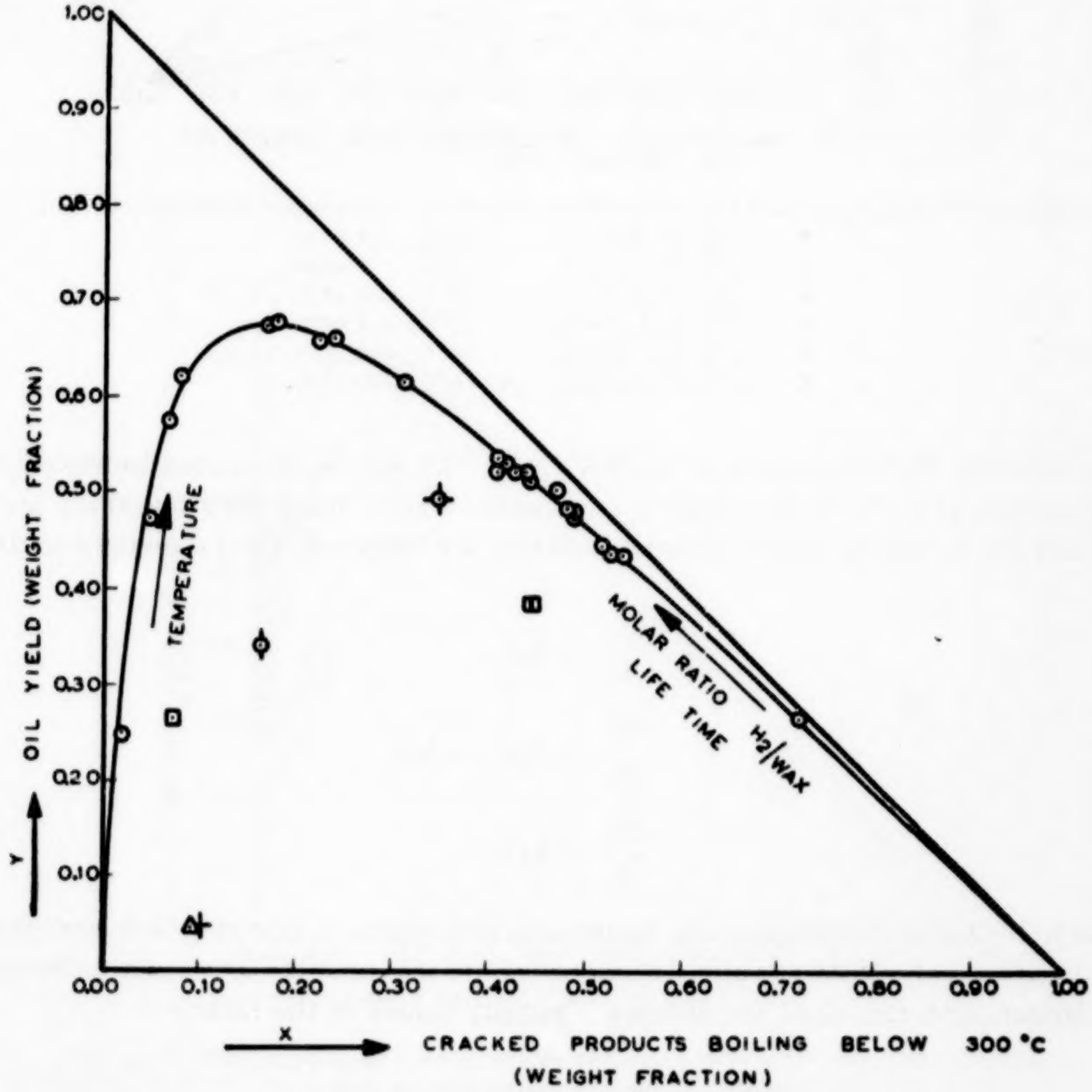


Fig. 94. Hydro-isomerization of paraffin wax.
⊙ Experiments with a platforming catalyst.
▲ + ⊡ ⌽ ⊕ ◫ Experiments with other catalysts.

up to 300°C and the residues subjected to a dewaxing treatment at —20°C.

To follow the reactions in a triangular diagram the following "components" were considered:

(1) unconverted wax, the wt. fraction of wax obtained in the dewaxing treatment;
(2) isomerized oil (the desired product), the wt. fraction of oil obtained after dewaxing;
(3) cracked products (by-products), the wt. fraction of low-boiling products obtained by distillation of the reaction products.

Fig. 94 shows the experimental results.

It appears that the experiments carried out with a platforming catalyst under different reaction conditions are all represented by *one* hyperbola (the values of a and b being: $a = 0.040$, $b = 0.9950$) in accordance with eqn. (87); the performance of the catalyst under the conditions mentioned above can thus be characterized by *two* constants, a and b. The use of other catalysts leads to other hyperbolas; some experiments with a few other catalysts are indicated in the diagram.

In this case it is a remarkable fact that experiments at different pressures and temperatures can be represented by one hyperbola. Fig. 94 immediately shows in which direction the product distribution will change when one of the process variables (the temperature, the molar ratio hydrogen: wax, the life-time of the catalyst) increases.

c. The chlorination of benzene[90]

This reaction was studied by MacMullin with anhydrous ferric chloride as a catalyst at 55°C; in the experiments the amount of chlorine introduced was varied with the change in reaction time.

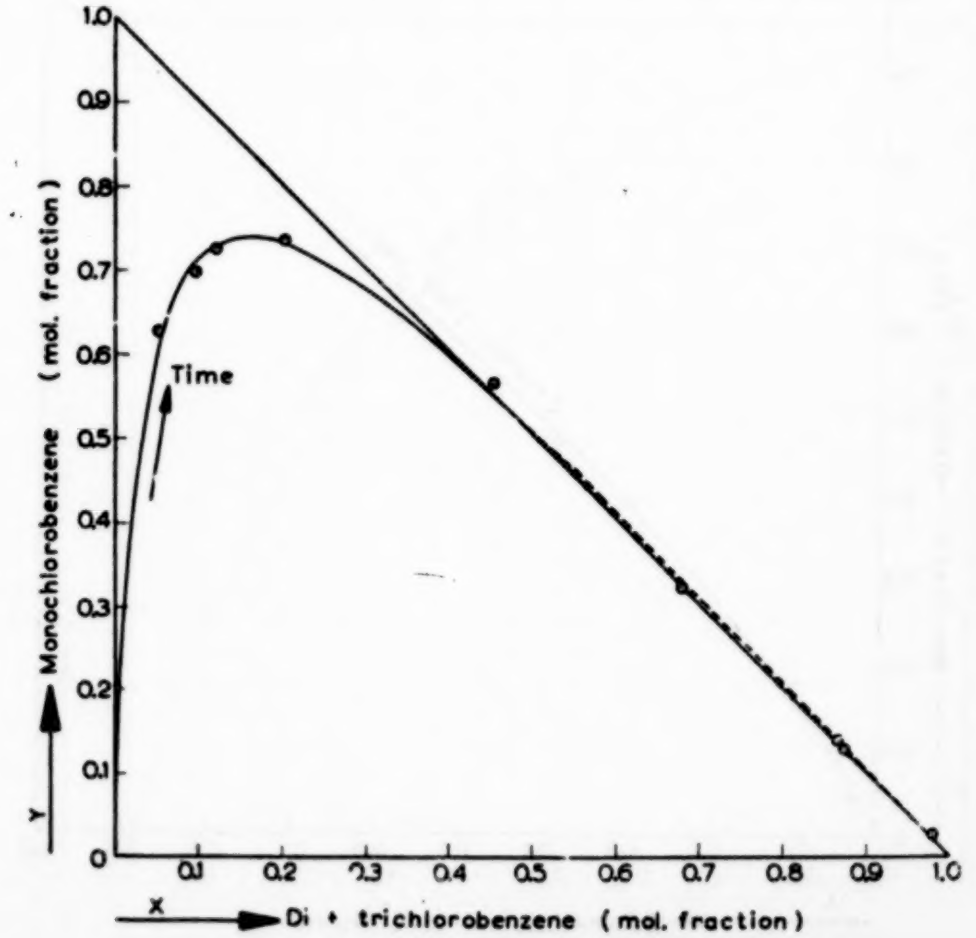


Fig. 95. Chlorination of benzene.

Fig. 95 gives the change in concentration of the components:

unconverted benzene,
monochlorobenzene,
(di + tri)chlorobenzene.

The curve can be represented by equation (87), in which $a = 0.0340$ and $b = 0.922$.

d. Selective hydrotreating of shale gasoline[91]

The simultaneous hydrogenation of olefins and thiophens in shale gasoline was studied by BERTIL HAMMAR[91]. The selectivity of the process under different conditions was judged by determining bromine numbers (Br) and sulphur contents (S) of the reaction products.

In Figs. 96, 97 and 98 reaction courses according to equation (88) are given for different temperatures; S_0 and Br_0 are the sulphur content and bromine number, respectively, in the starting materials.

4. SELECTION OF CATALYSTS

The experimental fact that the change of a reaction variable in a chemical process is connected with a change in the product distribution of the reactants according to eqn. (87) or eqn. (88) has an interesting consequence.

When only *one* experiment has been carried out with a certain catalyst, if eqn. (87)

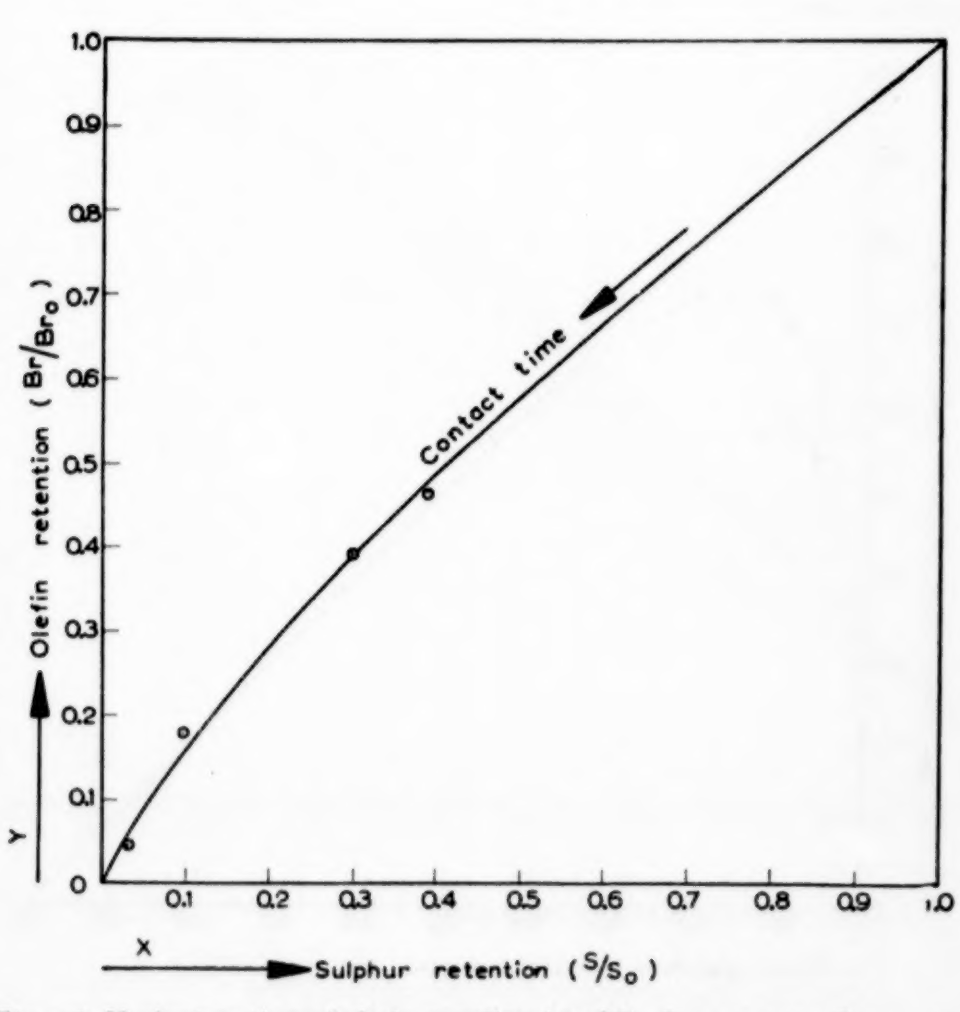


Fig. 96. Hydrotreating of shale gasoline (300°C). $S_0 = 0.340$, $Br_0 = 41.4$.

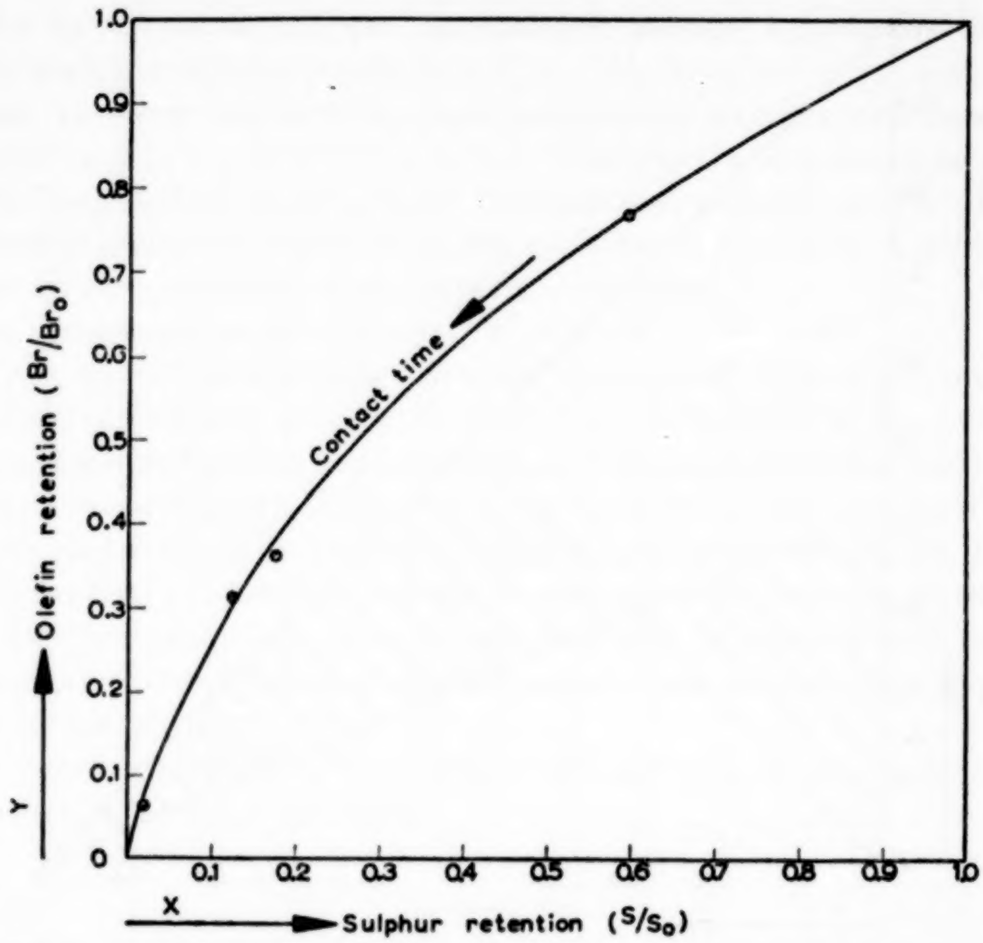


Fig. 97. Hydrotreating of shale gasoline (325°C). $S_o = 0.190$, $Br_o = 32.0$

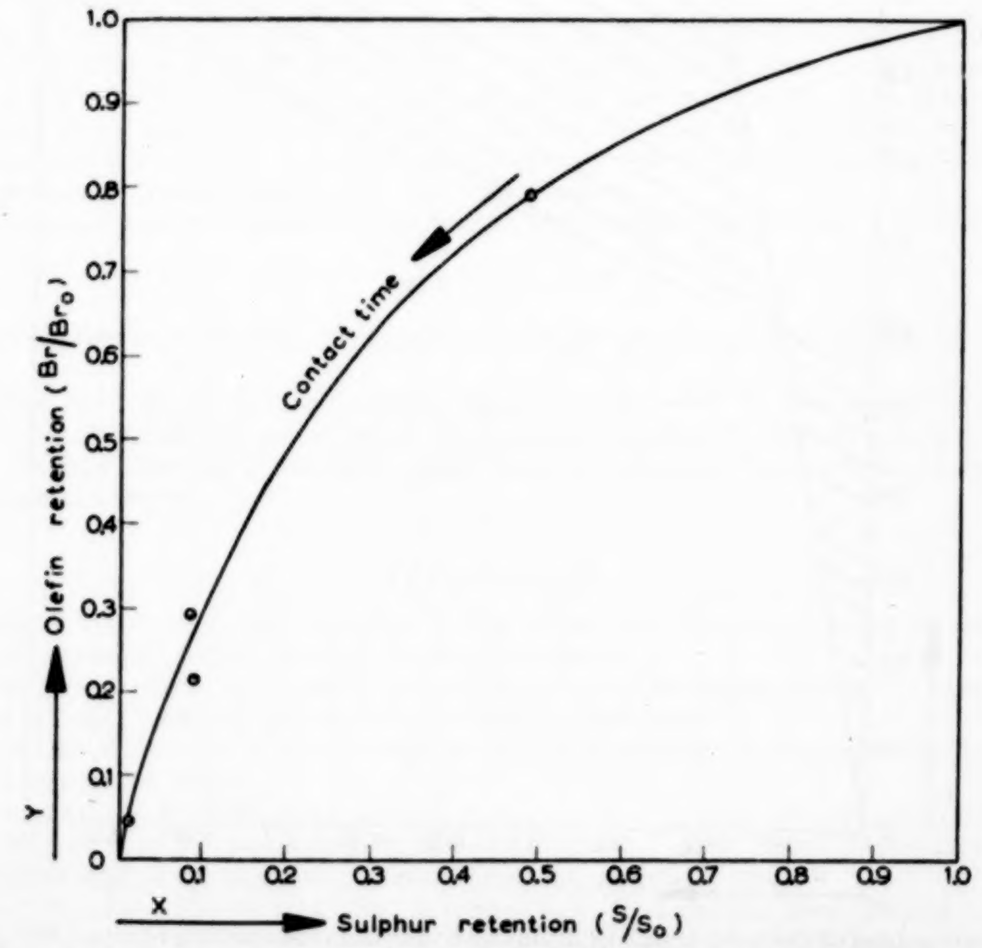


Fig. 98. Hydrotreating of shale gasoline (375°C). $S_o = 0.0678$, $Br_o = 17.7$.

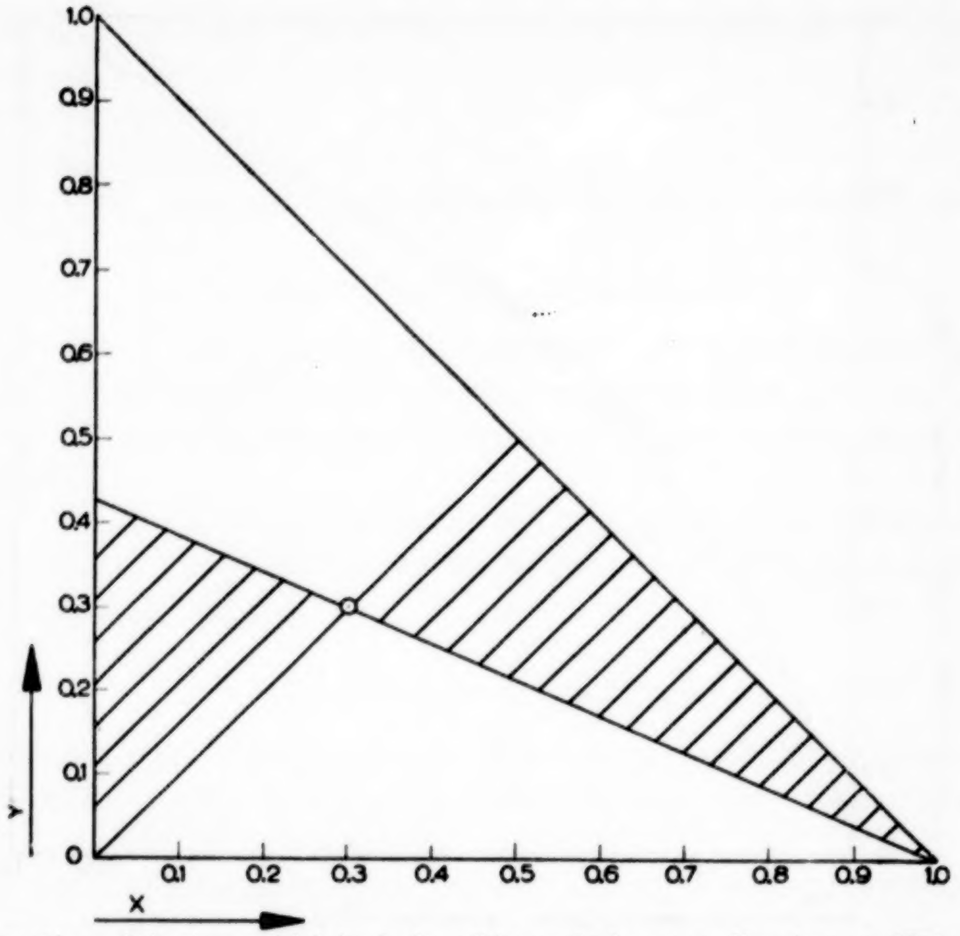


Fig. 99. Construction of the area which includes all hyperbolas according to eqn. (87), going through one experimental point and the angular points ($x = 0, y = 0$) and ($x = 1, y = 0$).

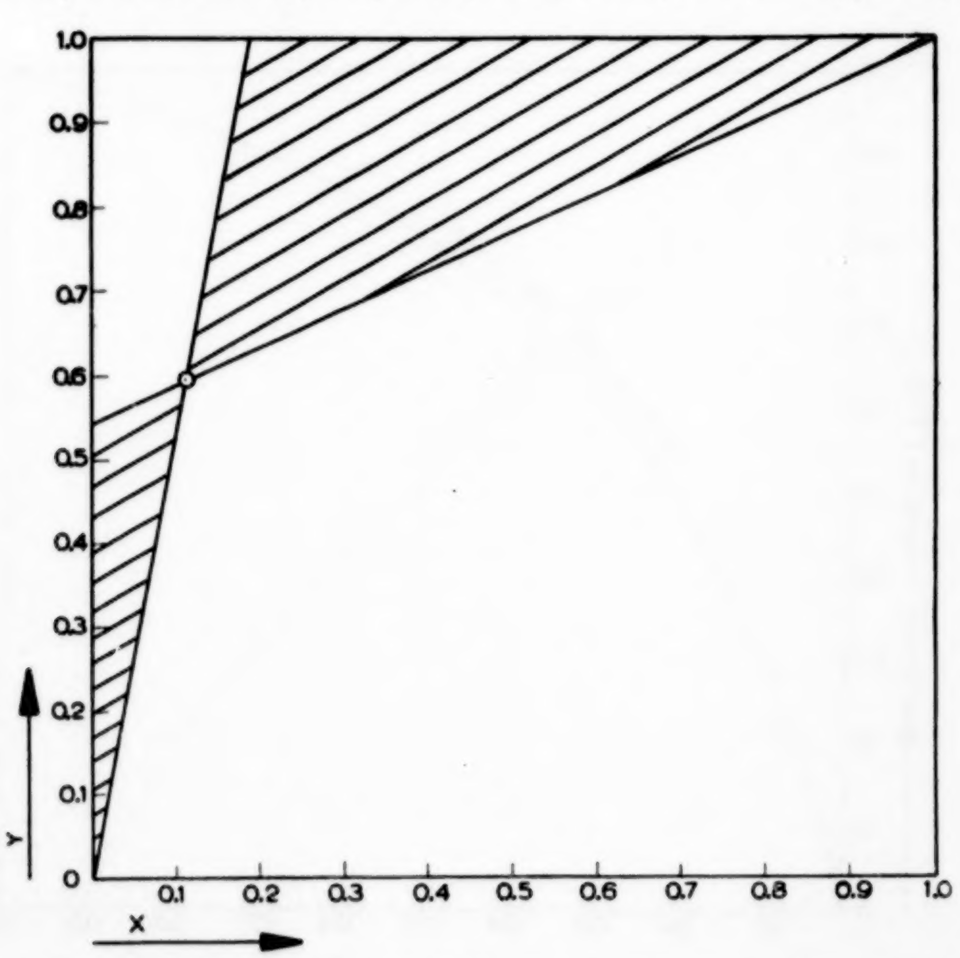


Fig. 100. Construction of the area which includes all hyperbolas according to eqn. (88) going through one experimental point and the angular points ($x = 0, y = 0$) and ($x = 1, y = 1$).

is valid, the hyperbola is not yet determined, infinite hyperbolas are possible, all going through the angular points ($x = 0, y = 0$), ($x = 1, y = 0$), and the experimental point. However, the limiting cases are given by straight lines drawn from the angular points ($x = 0, y = 0$) and ($x = 1, y = 0$) through the experimental point; these two straight lines enclose an area which represents all possible product distributions with the catalyst under investigation (*cf.* Fig. 99) when one reaction variable is changed with respect to the conditions of the experimental point.

The same considerations hold if eqn. (88) is valid, *cf.* Fig. 100.

When trying to find catalysts for chemical reactions of these types there is a convenient method of screening that can be used, if a proper choice of the components for the process under investigation has been made and the analysis of the reaction products has been directed accordingly. With each of the catalysts a single standard experiment is carried out and the results are plotted in the appropriate diagrams. The limiting reaction courses that are possible with the investigated catalysts can be directly compared and the most promising ones selected. A second experiment with each of these makes it possible to determine the values of *a* and *b* and construct the hyperbolas for a more precise comparison.

With this scheme a considerable saving of time and money may be achieved in the process research of complex reactions.

SUMMARY

The author's classical work on the ring analysis of mineral oils has been developed into a complete new system of investigation methods which have a specific character and are suitable for general application. The research field has become a very extensive one, and comes into contact with many branches of chemical industry.

The discussed methods may assist in gaining more insight into many natural products handled in industry and products prepared in factories. The applications of these methods are numerous; the purpose of this treatise is to enable everybody to become acquainted with them.

The introduction of the kinematic viscosity has been proved to be of high value for the investigation and characterization of mineral oils, it can replace in many cases the determination of the average molecular weight which now can be predicted.

The application of a new formula for the temperature dependence of the viscosity

$$\log \nu = \frac{A}{T^x} + B$$

has proved its significance for the investigation of many products, such as mineral oils, silicones and glasses.

Attention has been given to the characterization of chemical processes and of catalysts by simple equations of which the parameters allow more detailed studies of selectivity problems. This application may open up immediate possibilities of reducing the expenses of semi-industrial process development work.

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BOOK REVIEWS

Quantitative Organic Analysis, by J. S. Fritz and G. S. Hammond, John Wiley & Sons, Inc., New York, Chapman & Hall, Ltd., London. 1957, ix + 303 pp., £ 2,12,—.

Physical chemistry is of more importance to analysis than probably most practising analysts are aware; hence the increasing use of the physical chemical approach to the solving of problems of analysis is to be welcomed. Both of the authors are physical organic chemists who have obviously made good use of the inter-dependence of chemical kinetics and analysis.

The book constitutes mainly a review of recent analytical literature; it is essentially theoretical and, although a few practical examples are included in the last chapter, for the most part the student will have to refer to other text books (or the original references) for working details. The authors have drawn almost exclusively from the American literature and have often ignored earlier relevant work. The most glaring example of this is in the section on gas-liquid chromatography, where the pioneer work of A. T. James and A. J. P. Martin and of C. Phillips (*Analyst*, 1952) is given no mention. A rather misleading impression is given (p. 218) when it is stated that the maximum size of sample of liquids is about 1 ml. For the majority of columns used for gas-liquid chromatographic analysis the optimum amount is more of the order of 0.01 to 0.05 ml.

The amperometric method of Kolthoff and Harris for titration of thiols with a silver salt is quoted, but not criticisms of this method (R. L. Frank, P. V. Smith, F. E. Woodward, W. B. Reynolds and P. J. Canterino, *J. Polymer Sci.*, 3 (1948) 39; N. Strafford, F. R. Cropper and A. Hamer, *Analyst*, 75 (1950) 55).

The method for isocyanates of Siggia and Hanna mentioned in the book is similar in principle to the earlier one of Stagg (*Analyst*, 71 (1946) 557).

The inclusion of a chapter on elemental analysis (by well-known methods) is somewhat out of place in a book dealing with the use of fundamental principles in solving problems in organic analysis.

These criticisms in no way detract from the value of the book as a valuable stimulant to the student and research analyst, and as such it can be highly recommended. It presents an up-to-date picture of the main methods available for quantitative organic analysis, including a valuable section on spectrographic methods, and suggestions for the use of kinetics in analysis are especially valuable.

N. Strafford (Manchester)

A Short Course in Quantitative Analysis, par H. H. Willard, N. H. Furman et E. K. Bacon, D. van Nostrand Cy. Inc., New York, 1957, 233 pp., 2ème édition, $ 4.75; £ 1.15.—

L'importance de ce livre dont, autant que nous sachions, la première édition n'a pas été critiquée dans cette Revue, tient au fait qu'il nous reflète l'enseignement préparatoire de l'analyse quantitative aux Etats-Unis. Ecrit par des éminents spécialistes et, évidemment, fondé sur l'expérience de maintes années, il se restreint aux premiers principes et manipulations des dosages volumétriques et gravimétriques et en présente un aperçu remarquablement clair et exact, bien que très simple. Cela implique que c'est un livre pour les jeunes étudiants et leurs professeurs, et non pour les analystes plus expérimentés. On y trouve les chapitres bien connus sur la pesée, les burettes et pipettes, les indicateurs, les potentiels rédox et les principes de l'analyse gravimétrique, le tout à une échelle essentiellement ,,macro''. A la fin, en douze pages, on traite de l'analyse instrumentale, colorimétrique et potentiométrique sans entrer dans les détails. Le chapitre que nous apprécions le plus est celui sur l'évaluation mathématique des mesures scientifiques, les notions d'exactitude, de précision, d'erreurs et de déviations. Le nombre d'exemples des dosages gravimétriques est très restreint: chlorure, sulfate, fer et l'analyse plus ou moins complète du calcaire et du laiton.

Bref, ce n'est qu'une toute première introduction à l'analyse quantitative, mais une introduction très précieuse pour tous ceux qui en veulent maîtriser les principes ou qui sont chargés d'en enseigner les fondements traditionnels.

C. J. van Nieuwenburg (Delft)

Instrumental Analysis, par P. DELAHAY, xi + 384 pp., 137 figs., The MacMillan Co, New York, 1957, $ 7,90.

Ce livre constitue un ouvrage didactique destiné, principalement, aux étudiants débutants qui doivent se familiariser avec les méthodes physiques et physicochimiques de la chimie analytique.

Rédigé avec beaucoup de simplicité et surtout beaucoup de clarté, le livre traite successivement les méthodes suivantes: potentiométrie, polarographie et méthodes annexes, électrolyse, coulométrie, conductométrie, titrages à haute fréquence, spectroscopie, et spectrophotométrie, fluorimétrie, turbidimétrie et néphélométrie, spectres Raman, rayons X, spectrographie de masse et, enfin, quelques applications analytiques de la radiochimie.

A la fin de chaque chapitre le lecteur trouvera de nombreux problèmes numériques et des références bibliographiques judicieusement choisies. Enfin, le dernier chapitre du livre décrit brièvement un certain nombre d'expériences qui peuvent être exécutées au laboratoire assez facilement et qui aident l'étudiant à consolider les connaissances acquises.

Naturellement, le livre a été conçu selon les exigences du système d'enseignement américain. Nous estimons néanmoins qu'il serait également intéressant pour les étudiants européens, raison pour laquelle nous le leur recommandons vivement.

I. KAPETANIDIS (Genève)

ANNOUNCEMENT

GORDON RESEARCH CONFERENCES

The Gordon Research Conferences for 1958 will be held from 9 June to 29 August at Colby Junior College, New London, New Hampshire; New Hampton School New Hampton, New Hampshire and Kimball Union Academy, Meriden, New Hampshire.

The Conferences were established to stimulate research in universities, research foundations and industrial laboratories. This purpose is achieved by an informal type of meeting consisting of scheduled lectures and free discussion groups. Sufficient time is available to stimulate informal discussions among the members of a Conference. Meetings are held in the morning and in the evening, Monday through Friday, with the exception of Friday evening. The afternoons are available for participation in discussion groups as the individual desires. This type of meeting is a valuable means of disseminating information and ideas which otherwise would not be realized through the normal channels of publication and scientific meetings. In addition, scientists in related fields become acquainted and valuable associations are formed which result in collaboration and cooperative effort between different laboratories.

It is hoped that each Conference will extend the frontiers of science by fostering a free and informal exchange of ideas between persons actively interested in the subjects under discussion. The purpose of the program is not to review the known fields of chemistry but primarily to bring experts up to date as to the latest developments, analyze the significance of these developments, and te provoke suggestions as to underlying theories and profitable methods of approach for making new progress. In order to protect individual rights and to promote discussion, it is an established rule of each Conference that all information presented is not to be used without specific authorization of the individual making the contribution, whether in formal presentation or in discussion. No publications are prepared as emanating from the Conferences.

Individuals interested in attending a Conference are requested to send their applications to the Director. Each applicant must state the institution or company with which he is connected and the type of work in which he is most interested. Attendance at each Conference is limited to 100.

The complete program of the Conferences has been published in „Science" for February 28th.

Requests for attendance at the Conferences, or for any additional information, should be addressed to W. GEORGE PARKS, Director, Department of Chemistry, University of Rhode Island, Kingston, Rhode Island. From June 9 to August 29, 1958 mail should be addressed to Colby Junior College, New London, New Hampshire.

1958

GORDON RESEARCH CONFERENCES

New Hampton School
New Hampton, New Hampshire

ANALYTICAL CHEMISTRY SECTION

LOUIS GORDON, Chairman
JOHN MITCHELL, JR., Vice Chairman

11 *August.*

CHARLES N. REILLEY, Chelometric Analysis
EDWARD J. GRIFFITH, Thermogravimetry

12 *August.*

H. W. KIRBY, Progress Report on Radio Chemistry in Inorganic Analysis
G. DUYCKAERTS, Infrared Analysis of Solids

13 *August.*

HARLAN FOSTER, Nuclear Magnetic Resonance
Open Discussion

14 *August.*

W. KLYNE, Optical Rotatory Dispersion
E. W. ABRAHAMSON, Analysis of Reaction Intermediates

15 *August.*

J. B. NEILANDS, Enzymatic Reactions

ANALYSIS OF BISMUTH BASE ALLOYS

III. TERNARY ALLOYS CONTAINING URANIUM AND NEODYMIUM OR PRASEODYMIUM

by

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INTRODUCTION

Previous papers from this laboratory have described methods for the analysis of ternary bismuth base alloys with uranium and various other metals as minor constituents[1,2]. This paper reports the continuation of this work and deals with the determination of neodymium or praseodymium and uranium covering the range 0.2–5% of each minor constituent. No difficulty was expected in the determination of uranium since excellent volumetric[3], absorptiometric[4], and polarographic[5] methods are now available for this element. Bismuth is a troublesome interference in these methods, however, and its preliminary separation is desirable. Methods for the determination of the lanthanons have until recently been limited to the precipitation of the oxalate or hydroxide followed by ignition to the oxide[6]. These elements also form coloured complexes with such reagents as alizarin red S which are suitable for the determination of small amounts[7]. However, as with many other metals, the advent of ethylenediaminetetraacetic acid has enabled volumetric procedures to be developed for these elements. Volumetric methods are most attractive for the determination of alloying amounts of neodymium or praseodymium after separation of bismuth and uranium.

EXPERIMENTAL

Determination of neodymium and praseodymium

In preliminary experiments the titration of neodymium and praseodymium with EDTA was examined in detail. FLASCHKA[8] has described procedures by which lanthanons can be determined complexometrically; directly by titrating a boiling solution of pH 8–9 containing tartrate or citrate with eriochrome black T as indicator, indirectly by back titration of excess EDTA with a standard zinc solution using either eriochrome black T at pH 8–9 or the ferro-ferricyanide and 3,3′-dimethylnaphthidine indicator system at pH 5. The precision and reproducibility of the direct titration was not good and this still applied on using a mixed alizarin red S and methylene blue indicator[9]. In the case of the back titration methods, fading end-points were encountered, probably caused by the displacement of neodymium or praseodymium from its EDTA complex by zinc. Another back titration method using cobalt as the titrant in acetone-thiocyanate solution[10] also suffered from this fault and no variation in conditions could cure it. The most promising method was found to be based on manganous sulphate as back titrant at pH 8–8.5, using eriochrome black T as indicator[11]. Good recoveries were obtained for milligram amounts of neodymium or praseodymium, but the titration could not be applied in the presence of uranium which masked the colour change by combining with the indicator. This titration procedure was the best available for much of our work on this alloy system, but before the completion of this study, a quantity of the indicator xylenol orange[12] became available through the courtesy of Dr. R. PRIBIL. An examination showed that using this indicator, both neodymium and praseodymium could be titrated directly with EDTA at pH 5.6–6.1 in acetate buffered solution. The end-point was much sharper than with the manganese–eriochrome black T method and could be seen to within 0.01 ml 0.02M EDTA in 100 ml of solution. Small amounts of uranium could also be tolerated without affecting the end-point.

Using xylenol orange indicator, bismuth could be titrated directly with EDTA at pH 1.2–3.0 and then if ammonium acetate was added and the solution adjusted to pH 5.6–6.1 neodymium or praseodymium could also be titrated in the same solution. By using this procedure it was possible to determine 5% neodymium or praseodymium in bismuth to an accuracy of better than ± 1%, but this accuracy could not be maintained with lower levels of lanthanon so a separation was still considered necessary.

An examination of methods for the separation of bismuth

Since bismuth causes interference in the procedures for the determination of uranium, neodymium and praseodymium, the preliminary removal of this alloying constituent proved to be essential. In early experiments the possibility of employing an ion exchange procedure was examined, since this type of separation had proved valuable in the analysis of the bismuth–uranium–thorium system[2]. The behaviour of neodymium and praseodymium in chloride solutions with the anion exchange resin Deacidite FF is similar to that of thorium[13], and in the analysis of synthetic bismuth–uranium–neodymium solutions a 5N hydrochloric acid solution was passed through a suitable column of this resin. The eluant containing the neodymium was evaporated to fumes of sulphuric acid and any organic matter in the solution removed by wet oxidation with nitric acid. Then the neodymium content was determined by the back titration procedure employing manganous sulphate with eriochrome black T as the indicator. Difficulty was frequently encountered in the detection of the titration end-point after this separation, the colour change being obscured by the formation of permanent foreign colours by trace constituents with the eriochrome black T. This effect could not be due to residual organic matter in solution since it still persisted after the use of dry ignition at 850°C, instead of wet oxidation, the resultant neodymia being readily dissolved in nitric acid before titration with EDTA.

Macro amounts of bismuth can be removed from many other metals by volatilisation of its tribromide, as described in a method for the determination of the uranium content of bismuth alloys[14]. Since both neodymium and praseodymium bromides are relatively involatile, the separation of bismuth from these elements should be possible. In experiments carried out to examine this procedure, suitable mixtures of bismuth nitrate and neodymium nitrate solutions were treated with 15% v/v bromine in hydrobromic acid mixture and heated in a hot air bath at 350°C until no more bismuth tribromide volatilised. This process was repeated with more of the bromine–hydrobromic acid mixture to obtain complete removal of the bismuth. The residue was dissolved in dilute nitric

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acid and the neodymium content determined by the manganous sulphate back-titration procedure. End-points in this titration were much sharper after this method of separation of bismuth, but they were still not entirely satisfactory since occasional solutions failed to give any detectable colour change at the end-point. An examination of typical residues from the bromination showed that small amounts of bismuth were left behind even after several treatments with bromine - hydrobromic acid mixture, the amounts varying roughly directly with the neodymium present. The presence of these very small amounts of bismuth could possibly account for the difficulty in detecting the end-point of the titration.

The applicability of solvent extraction for the removal of bismuth was next examined. During experiments to mask small amounts of bismuth not removed by volatilisation as tribromide, it was found that this element could be readily extracted into a chloroform solution of diethylammonium-diethyldithiocarbamate(DETC). This extraction could be applied to solutions as strong as 3*N* in nitric acid and could be used to remove macro amounts of bismuth from aqueous solutions. The solubility of the bismuth-DETC complex in chloroform is high, about 1 g of bismuth being extracted by 50-60 ml 5% w/v DETC in chloroform. After extraction no difficulty was met in the detection of end-points in the EDTA titration procedure for the determination of neodymium or praseodymium. Uranium remained quantitatively in the aqueous solution, if the extraction was carried out from a solution *N* in nitric acid and this separation appeared suitable for the preliminary removal of bismuth in the analysis of alloy samples.

Determination of uranium

The uranium - diethyldithiocarbamate complex has been employed for the absorptiometric determination of uranium in both aqueous[16] and chloroform[4] solutions. The range of pH for the formation and extraction of the complex is rather limited and its

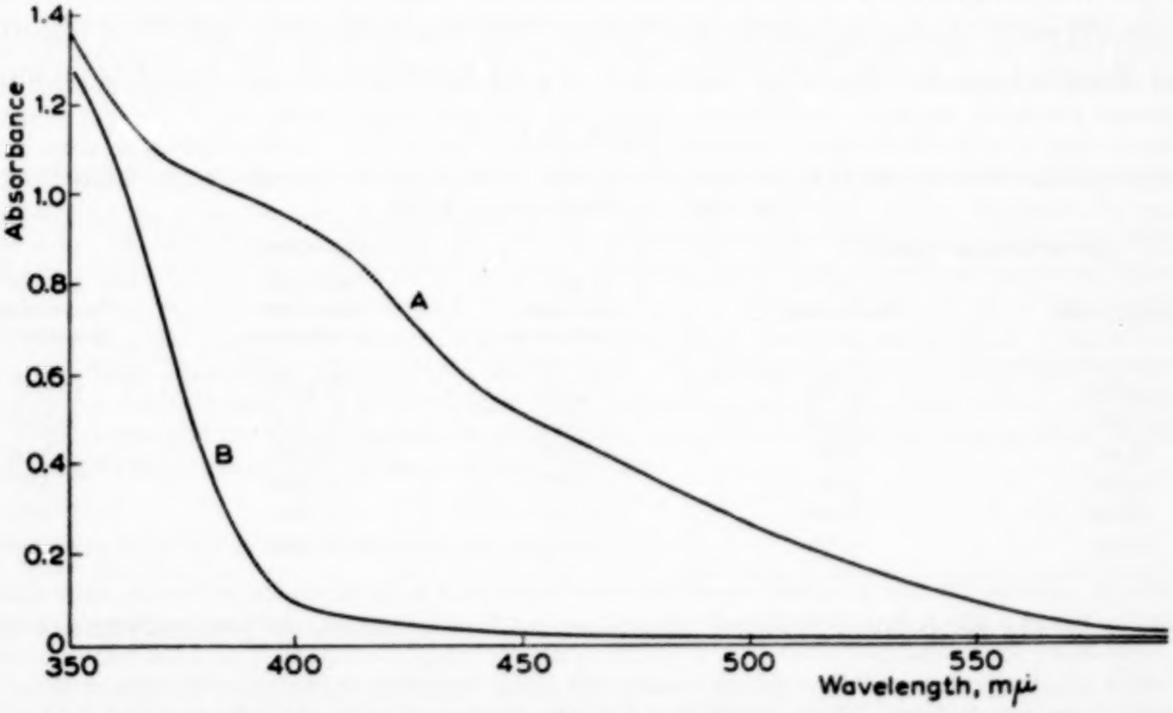

Fig. 1. Absorption spectra of uranium-diethyldithiocarbamate in chloroform.
A. 5 mg uranium in 100 ml 0.25% diethyldithiocarbamate in chloroform.
B. 0.25% diethyldithiocarbamate in chloroform.

stability is not great, with the result that this method has not been used very much. It was considered, however, that further study was desirable, especially since there was a possibility of applying the extraction of uranium-DETC, after removing bismuth, as both a separation and a determination at the same time, thus making a great economy in the time needed for an analysis.

To study the absorption characteristics of the uranium-DETC complex, 40 ml of an aqueous solution containing 5 mg uranium and 2 g of ammonium acetate was shaken with 50 ml of 0.5% w/v DETC in chloroform. After separation of the organic layer it was diluted to 100 ml with chloroform and the absorption spectrum of the solution plotted, using a Uvispek spectrophotometer, against a water blank. The resultant spectrum is shown in Fig. 1, as is also that of 0.25% w/v DETC in chloroform. The greatest difference in absorption occurs at 400-420 mμ, and for routine determinations a Spekker absorptiometer fitted with Ilford 601 filters is suitable.

To test the effect of the pH of the aqueous solution on the development of the uranium-DETC complex and also the stability of the chloroform extract, solutions were prepared containing 5 mg of uranium and 10 ml of 20% w/v ammonium acetate solution in a total volume of 40 ml. After adjustment to the required pH value, the solution was shaken with 25 ml of 0.5% DETC in chloroform in a 100 ml separating funnel. The layers were allowed to separate and the chloroform layer run off into a 100 ml graduated flask using two separate 5 ml portions of chloroform as washes. Further extractions were made with 15 ml and than 10 ml of 0.5% DETC in chloroform and the combined organic extracts diluted to 100 ml with chloroform. The absorbancy of the resultant solution was measured in 1 cm cells with the Spekker absorptiometer and measurements repeated at intervals of time. The results of this study are given in Table I and it can be seen that no great error is introduced if absorbancy measurements are taken within 30 min of the start of the extraction from solutions originally pH 5.5-7. In applying this method to solutions also containing neodymium or praseodymium, it was found that a pH in the range 5.5-6 was desirable since at higher pH's there is some danger of these constituents precipitating from solution. The solution of U-DETC in chloroform obeyed Beer's Law in the range from 0-6 mg of uranium in 100 ml of solution.

TABLE I

VARIATION OF THE STABILITY OF THE U-DETC COMPLEX IN CHLOROFORM WITH THE pH OF THE AQUEOUS SOLUTION

pH of aqueous solution		*Absorbancy*		
Initial value	*Final value*	*8 min after start of extraction*	*20 min after start of extraction*	*30 min after start of extraction*
4.80	4.85	0.516	0.458	0.446
5.00	5.05	0.544	0.512	0.506
5.40	5.60	0.558	0.558	0.554
5.60	5.90	0.568	0.564	0.567
6.00	7.00	0.562	0.560	0.560
7.00	7.75	0.555	0.552	0.552

Procedure for the analysis of bismuth, uranium and neodymium or praseodymium ternary alloys

As a result of the above investigations, the following methods were developed for the analysis of bismuth base alloys containing uranium and neodymium or praseodymium as minor constituents.

Reagents

0.02*M EDTA solution*. Dissolve 7.45 g of EDTA disodium salt in deionised water and dilute to 1 l. Standardise against a solution of A.R. zinc metal in hydrochloric acid, using eriochrome black T indicator at pH 8–9.

0.02*M Manganous sulphate solution*. Dissolve 3.40 g of $MnSO_4.H_2O$ in water and dilute to 1 l. Standardise against EDTA solution using eriochrome black T indicator at pH 8–9 in the presence of 100 mg ascorbic acid.

0.1% *Eriochrome black T solution*. Dissolve 50 mg of the dye in 50 ml of 95% alcohol. This solution does not keep and should be renewed about once a week.

0.1% *Xylenol orange solution*. Dissolve 50 mg of the solid in 10 ml of alcohol and dilute to 50 ml with water.

5% *DETC solution*. Dissolve 50 g of diethylammonium diethyldithiocarbamate in 1 l of A.R. chloroform and keep in a dark glass bottle. Dilute suitably with chloroform when weaker solutions are needed.

Other reagents of A.R. quality.

METHODS

Solution of the alloy

Warm the sample with 25% v/v nitric acid until solution is complete and then boil for 2–3 min to expel nitrous fumes. Cool and dilute to a suitable volume, adding more nitric acid if necessary to make the final solution approximately 1*N* in acid.

Determination of bismuth and rough determination of lanthanon

Take an aliquot containing about 100 mg of bismuth and dilute to 100 ml with water. Adjust to about pH 1.5, add 2–3 drops of 0.1% xylenol orange solution and titrate with 0.02*M* EDTA solution until the colour changes from pink to yellow. Now add 10 ml 20% v/v ammonium acetate solution, adjust to pH 5.6–6 and again titrate with 0.02*M* EDTA solution until the pink colour, which was restored on raising the pH, changes to yellow. From the first titration calculate the bismuth content from the expression 1 ml 0.02*M* EDTA ≡ 4.18 mg bismuth. From the second titration calculate the neodymium or praseodymium content from the expression 1 ml 0.02*M* EDTA = 2.885 mg neodymium or 2.818 mg praseodymium.

Determination of uranium

Take an aliquot of the alloy solution containing up to 1 g of the sample in 25 ml and transfer to a 100 ml separating funnel. Dilute to 25 ml, if necessary, with *N* nitric acid and add 50 ml 5% w/v DETC solution. Shake for 30 sec and allow the layers to separate. Run off the lower chloroform layer and discard. Repeat the extraction with 5 ml portions of 5% DETC solution until the resultant chloroform layer is colourless, signifying the complete removal of bismuth. Extract the aqueous solution with 20 ml chloroform and discard the chloroform layer. Add 10 ml of 20% w/v ammonium acetate solution to the solution in the separating funnel, followed by the dropwise addition of 0.880*N* ammonia until the solution has a pH of 5.5–6 as shown by indicator paper. Extract the uranium with 25 ml 0.5% DETC solution (use 1% DETC solution if more than 20 mg uranium is present) and transfer the chloroform layer to a 100 ml graduated flask using small volumes of chloroform for washing. Repeat the extraction with 15 ml and then 10 ml of DETC solution. Dilute the combined extracts with chloroform to the mark. If the solution contains more than 6 mg of uranium per 100 ml, take a suitable aliquot and dilute with chloroform. Measure the absorbancy of the solution in a 1 cm cell against a water blank using a Spekker absorptiometer fitted with Ilford 601 filters. Determine the uranium content by reference to a calibration graph prepared with standard uranium solutions covering the range 0–6 mg uranium.

Determination of neodymium or praseodymium

Transfer the aqueous solution from the uranium determination to a 250 ml beaker, dilute to 100 ml and add enough 0.02*M* EDTA solution to complex the lanthanon and leave a small excess. Add 100 mg ascorbic acid, 4–5 drops 0.1% eriochrome black T solution and adjust to pH 8–8.5. Titrate with 0.02*M* manganous sulphate solution until the colour of the solution changes from blue to red. Alternatively, adjust the solution to pH 5.6–6, add 2–3 drops 0.1% xylenol orange solution and titrate with 0.02*M* EDTA solution until the colour changes from pink to yellow.

1 ml 0.02*M* EDTA = 2.885 mg Nd or 2.818 mg Pr.

RESULTS AND CONCLUSIONS

The procedures described above were tested on synthetic solutions representing alloy compositions in the expected ranges. These solutions were prepared by combining aliquots of standard bismuth, uranium and neodymium or praseodymium nitrate solutions prepared from high purity materials dissolved in nitric acid. The neodymium nitrate solution was prepared from 'Specpure' oxide and standardised gravimetrically by precipitation as oxalate followed by ignition to Nd_2O_3 at 850°C. Similarly with the praseodymium nitrate solution which was weighed as Pr_6O_{11}. These gravimetric standardisations agreed to within 0.5% of that obtained by titration with EDTA. The uranium nitrate solution was prepared by dissolving freshly ignited 'Specpure' U_3O_8 in nitric acid and the bismuth nitrate solution by dissolving high purity metal (>99.99% purity) in dilute nitric acid. The satisfactory results obtained for the analysis of these solutions are given in Tables II and III.

TABLE II

ANALYSIS OF SYNTHETIC MIXTURES OF BISMUTH, URANIUM AND NEODYMIUM

Synthetic composition		*Composition by analysis*	
% Nd	*% U*	*% Nd*	*% U*
0.19	4.75	(i) 0.19	4.66
		(ii) 0.18	4.72
0.95	2.42	(i) 0.945	2.37
		(ii) 0.95	2.46
2.37	0.965	(i) 2.36	0.965
		(ii) 2.44	0.955
4.67	0.19	(i) 4.68	0.19
		(ii) 4.68	0.195

TABLE III

ANALYSIS OF SYNTHETIC MIXTURES OF BISMUTH, URANIUM AND PRASEODYMIUM

Synthetic composition		*Composition by analysis*	
% Pr	*% U*	*% Pr*	*% U*
0.22	4.76	(i) 0.21	4.66
		(ii) 0.21	4.77
2.30	0.97	(i) 2.28	0.96
		(ii) 2.27	0.97
4.42	0.24	(i) 4.42	0.24
		(ii) 4.41	0.24

A series of actual metallurgical alloy samples was next analysed by the procedure described and the satisfactory total composition figures show the suitability of the method.

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TABLE IV

ANALYSIS OF BISMUTH, URANIUM, NEODYMIUM ALLOYS

Sample No.	*% Bi*	*% Nd*	*% U*	*Total*
1	91.3	4.1	4.4	99.8
2	92.1	4.0	3.8	99.9
3	92.0	3.9	3.6	99.5
4	94.2	3.4	2.5	100.1

In conclusion it may be said that the use of diethylammonium diethyldithiocarbamate has proved to be very useful for the quick separation of bismuth in the analysis of bismuth base alloys. Combined with the determination of neodymium and praseodymium by titration with EDTA and the absorptiometric determination of uranium as its diethyldithiocarbamate, this procedure has been made so rapid that a complete analysis of a ternary alloy can be completed in 30 min after solution of the sample.

SUMMARY

Procedures are described for the analysis of bismuth base alloys containing 0.2–5% of uranium and 0.2–5% of neodymium or praseodymium. Bismuth is first separated from a solution of the alloy in *N* nitric acid by extraction with diethylammonium diethyldithiocarbamate in chloroform, followed by the separation of uranium with the same reagent from an acetate buffered solution of pH 5.5–6.0. The uranium determination is completed by measuring the absorbancy of its diethyldithiocarbamate complex in chloroform. The neodymium or praseodymium is determined by titration with EDTA of the aqueous solution remaining after the separation of bismuth and uranium, using xylenol orange indicator in solutions of pH 5.6–5.8. EDTA is also used to determine the bismuth by direct titration of a separate aliquot of the sample solutions.

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SEPARATIONS INVOLVING SULPHIDES

V. SEPARATION OF BISMUTH, CADMIUM AND INDIUM FROM VARIOUS OTHER ELEMENTS THAT FORM THIOSALTS

by

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In earlier publications[1,2] it was shown that 2*N* sodium sulphide reagent[3] can be efficiently used in the separation of metals like arsenic, molybdenum, tellurium and rhenium, etc., from mercury and lead. In this paper, similar procedures are given for separating bismuth, cadmium and indium from the various other elements that form thiosalts.

The methods adopted in separating the elements may be very briefly classified as follows:

(1) One of the elements was precipitated and weighed as sulphide after decomposing its thiosalt, and the other was estimated as sulphide in the filtrate.

(2) In one portion of the solution, both elements were precipitated as sulphides and weighed together. In another portion only one element was precipitated (by altering the conditions) and weighed as sulphide.

(3) In two different portions, the two metals were separately precipitated as sulphide under different conditions.

EXPERIMENTAL

Separation of tellurium from bismuth

Measured volumes of standard solutions of bismuth[4] and tellurite[5] were mixed and the free acid neutralized with ammonium hydroxide. In one set of experiments the solution was treated with 55–70 ml of 2*N* sodium sulphide reagent followed by 10–15 g of ammonium acetate (solid) in the cold. The mixture was shaken for 1 min to complete the precipitation of bismuth as trisulphide. The precipitate of bismuth trisulphide was filtered through a weighed sintered glass crucible (porosity 4), washed thoroughly with water and alcohol, dried in an air-oven at 105° for 1 h and weighed. In another set of experiments, after adding sodium sulphide reagent, the mixture was treated with enough 3*N* hydrochloric acid to give a final acidity of about 1*N*. The mixture was heated to boiling and allowed to cool to room temperature. The precipitate of mixed sulphides was then filtered through a weighed sintered glass crucible, washed thoroughly with water, dried in an air-oven at 100-105° for 1 h and weighed.

30–70 mg of bismuth could be separated from 40–60 mg of tellurium. Bismuth was recovered with an accuracy of 0.0 to -0.30% and tellurium -0.13 to $+0.14\%$.

Separation of molybdenum or antimony from bismuth

These separations were done as described above using standard solutions of bismuth and ammonium molybdate[6] or potassium hydrogen antimonate[7]. In the case of molybdenum, the precipitate of the mixed sulphides was washed thoroughly with water, alcohol and ether successively, sucked dry at a filter pump for 15 min, dried in a vacuum desiccator for 1 h and weighed.

25–35 mg of bismuth could be separated from 40–50 mg of molybdenum or 35–45 mg of antimony(V). Bismuth was recovered with an accuracy of 0.0 to —0.3%, molybdenum 0.0 to —0.23% and antimony 0.0 to —0.27%.

Separation of rhenium from bismuth

Standard solutions of bismuth and perrhenate[8] were used. Bismuth was estimated as Bi_2S_3, following the procedure given for the separation of bismuth from tellurium. In the second series of experiments, enough 12*N* hydrochloric acid was used to give an 8*N* solution and 10–15 g of ammonium sulphate (solid) were added. The mixture was heated to boiling to dissolve bismuth trisulphide and to completely precipitate rhenium as Re_2S_7. The latter was washed with hot 8*N* hydrochloric acid, water, alcohol and ether successively, dried in a vacuum desiccator for half an hour and weighed.

Bismuth cannot be estimated as Bi_2S_3 in the filtrate from rhenium heptasulphide because too high results are obtained owing to contamination with sulphur.

25–35 mg of bismuth could be separated from 20–30 mg of rhenium. Bismuth and rhenium were recovered with an accuracy of 0.0 to —0.3%.

Separation of platinum, gold or selenium from cadmium

Standard solutions of cadmium sulphate[4] and platinic chloride[7], gold chloride[9] or potassium selenite[10] were used. The precipitate of cadmium selenite was dissolved in ammonia (sp gr. 0.88). The procedure given in the second series of experiments for the separation of bismuth from rhenium was followed in each separation, but 10–15 g of ammonium acetate (solid) were added in place of ammonium sulphate in the case of platinum. The concentration of the acid in the resulting mixture was adjusted to a little above 6*N* to keep cadmium in solution. The precipitated sulphide was washed with hot 6*N* hydrochloric acid (retaining the filtrate for the estimation of cadmium) and then thoroughly with water. The precipitate of platinum or gold sulphide was further washed with alcohol and ether, dried at 105° and weighed. The precipitate of selenium sulphide, after washing only with water, was dried at 95° before being weighed.

The filtrate was concentrated to about 25 ml, the free acid neutralized with ammonia, the solution cooled in ice and then treated with 20–25 ml of sodium sulphide reagent followed by a large excess of 6*N* acetic acid. The mixture was heated to boiling, the precipitate of cadmium sulphide allowed to settle, filtered through a weighed sintered glass crucible, washed thoroughly with alcohol and ether successively, dried at 105° for 1 h and weighed.

20–60 mg of cadmium could be separated from 15–25 mg of platinum, 20–30 mg of gold, or 30–80 mg of selenium. The metals were recovered with an accuracy of

Cd 0.0 to —0.37% and Pt 0.0 to —0.35%;
Cd 0.0 to —0.19% and Au +0.05 to —0.32%;
Cd 0.0 to —0.14% and Se +0.06 to 0.11%.

Separation of rhenium, arsenic, molybdenum or tellurium(VI) from cadmium

Standard solutions of cadmium sulphate and potassium perrhenate, potassium arsenate[11], ammonium molybdate or potassium tellurate[12] were used. The precipitate of cadmium arsenate or molybdate was dissolved in the minimum quantity of ammonia and that of cadmium tellurate in glacial acetic acid. The procedure given for the separation of bismuth from rhenium was applied but no ammonium acetate was added. In the second series of experiments the final concentration of the acid was adjusted to a little above 6*N* to keep cadmium in solution. The precipitate of rhenium heptasulphide, arsenic pentasulphide or molybdenum trisulphide, was treated with alcohol and ether, dried in a vacuum desiccator and weighed. TeS_3 was washed only with water, dried at 105° and weighed. Cadmium can also be estimated as sulphide in the filtrate from rhenium heptasulphide, arsenic pentasulphide, molybdenum trisulphide or tellurium trisulphide, but this takes more time.

20–65 mg of cadmium could be separated from 30–60 mg of rhenium, 10–30 mg of arsenic, 20–50 mg of molybdenum or 20–45 mg of tellurium. The metals were recovered with an accuracy of

Cd —0.37 to +0.23% and Re —0.23 to +0.02%;
Cd 0.0 to —0.36% and As 0.0 to —0.19%;
Cd 0.0 to —0.4% and Mo +0.09 to —0.18%;
Cd 0.0 to —0.2% and Te^{+6} 0.0 to —0.2%.

Separation of tellurium(IV) from cadmium

Standard solutions of cadmium sulphate and potassium tellurite were used. The precipitate of cadmium tellurite was dissolved in the minimum quantity of hydrochloric acid (since it is not soluble in acetic acid). In one set of experiments, 6*N* acetic acid was used to precipitate the two

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sulphides together. In the second series of experiments, the procedure given for the separation of selenium from cadmium was followed. TeS_2 was dried at 105° for 1 h and weighed.

20–130 mg of cadmium could be separated from 20–80 mg of tellurium. Cadmium was recovered with an accuracy of +0.15 to −0.34 and tellurium +0.17 to −0.19%.

Separation of platinum, gold, rhenium, arsenic, molybdenum, antimony, tellurium or selenium from indium

Standard solutions of indium sulphate[4] and platinic chloride, gold chloride, potassium perrhenate, potassium arsenate, ammonium molybdate, potassium hydrogen antimonate[7], potassium tellurate, potassium tellurite or potassium selenite were used. If any precipitate was obtained on mixing the solutions it was dissolved in the minimum quantity of hydrochloric acid. The procedure given for the separation of platinum from cadmium was followed. Ammonium acetate was added only in the precipitation of platinum and rhenium as sulphide. The thiosalts of platinum, gold, rhenium, arsenic and tellurium(VI) were decomposed with 12*N* hydrochloric acid, the final acidity being adjusted to about 6*N*. Those of molybdenum, antimony (V) and tellurium (IV) were decomposed with 3*N* hydrochloric acid and the final concentration of the acid was adjusted to about 1*N*. The precipitated sulphides of these metals were washed with hot 1*N* hydrochloric acid (not 6*N* HCl) and subjected to suitable treatment before weighing as given above in the separations of bismuth and cadmium. In the filtrate, indium was estimated as In_2S_3 by following the procedure outlined for cadmium.

Instead of estimating indium in the filtrate, it can also be estimated directly in another portion of the solution by adding an excess of 5*N* ammonium sulphide reagent. This method is applicable only to separations involving molybdenum, arsenic, rhenium, tellurium(IV) or tellurium(VI).

15–25 mg of indium could be separated from 15–25 mg of platinum, 25–30 mg of gold, 20–30 mg of rhenium, 30–35 mg of arsenic, 40–45 mg of molybdenum, 35–45 mg of antimony, 35–50 mg of tellurium(VI), 45–55 mg of tellurium(IV) or 65–80 mg of selenium(IV). The metals were recovered with an accuracy of

In 0.0 to −0.4% and Pt 0.0 to −0.35%;
In 0.0 to −0.4% and Au 0.0 to −0.37%;
In 0.0 to −0.32% and Re 0.0 to −0.27%;
In 0.0 to −0.4% and As +0.04 to −0.19%;
In 0.0 to −0.4% and Mo 0.0 to −0.16%;
In 0.0 to −0.32% and Sb^{+5} 0.0 to −0.20%;
In 0.0 to −0.4% and Te^{+6} 0.0 to −0.31%;
In 0.0 to −0.32% and Te^{+4} 0.0 to 0.31%;
In 0.0 to −0.32% and Se^{+4} 0.0 to 0.14%.

NOTE

Separation of arsenic, platinum, gold or selenium from bismuth

When a solution containing arsenic and bismuth is treated with an excess of 2*N* sodium sulphide reagent followed by 10–15 g of ammonium acetate (solid), bismuth is completely precipitated as Bi_2S_3, thus affording a method for the direct estimation of the metal; however, the decomposition of the thiosalt of arsenic with 12*N* hydrochloric acid gives high results for arsenic owing to coprecipitation of bismuth. In the case of platinum, gold and selenium, the slow decomposition of the thiosalts of these metals on exposure to air or on standing, leads to the contamination of the precipitate of bismuth trisulphide with these metals and makes the method inapplicable to quantitative analysis.

Separation of antimony from cadmium

When a solution containing cadmium and antimony is treated with 2*N* sodium sulphide reagent, the thiosalt of antimony is not decomposed completely by 6*N* acetic acid, if 1*N* hydrochloric acid is used, both antimony and cadmium are completely precipitated as sulphides, but the cadmium sulphide thus precipitated has a marked tendency to peptize on washing with water. Therefore, the method does not find application in quantitative analysis.

Separation of tin from bismuth, cadmium or indium

In this case, the precipitate of stannic sulphide obtained by decomposing its thiosalt with acetic acid or dilute hydrochloric acid is highly gelatinous in character and has a marked tendency to peptize on washing with water. The method is, therefore, not applicable to the separation of tin from bismuth, cadmium or indium in quantitative analysis.

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SUMMARY

It has been shown that 2N sodium sulphide reagent can be successfully used in separating tellurium, molybdenum, antimony or rhenium from bismuth; platinum, gold, selenium, rhenium, arsenic, molybdenum or tellurium from cadmium; platinum, gold, selenium, rhenium, arsenic, molybdenum, tellurium or antimony from indium.

It is not possible to separate quantitatively arsenic, platinum, gold or selenium from bismuth; antimony from cadmium; and tin from bismuth, cadmium or indium.

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THE DETERMINATION OF MICROGRAM AND SUB-MICROGRAM AMOUNTS OF BORON

II. THE SEPARATION OF BORON BY DISTILLATION AND THE EVAPORATION OF DISTILLATES

by

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INTRODUCTION

Absorptiometric methods for the determination of microgram amounts of boron, when present in small alkaline residues in platinum dishes, were described in the previous paper[1]. The purpose of the present account is to present the general principles and methods used in the laboratories of the United Kingdom Atomic Energy for the separation of boron from samples by distillation and the subsequent evaporation of these distillates. In addition, the opportunity is taken to outline the precautions necessary to prevent or minimise contamination by boron introduced from apparatus and reagents. When working with quantities of boron of a few micrograms or less, the control of contamination assumes major importance, as this element is of common occurrence in nearly all chemicals and can be picked up from nearly all laboratoryware.

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EVAPORATION OF METHANOLIC DISTILLATES

All distillation techniques given later have been designed to remove the boron from a sample in less than 100 ml (generally 50 ml) of methyl alcohol. As the curcumin (or other) methods require that the boron, as borate, be present in a dry residue, the problem arises of evaporating a methyl alcohol distillate without again volatilising the boron as methyl borate. The presence of alkali alone is not sufficient, as is generally the case when macro amounts of borate are involved, unless the alkali is present in impracticably large amounts. When only some tens of milligrams of sodium hydroxide are acceptable, as is the case when a curcumin method is to be employed, serious boron losses occur unless water is also added to the distillates in an amount equal to at least half of the volume of the methyl alcohol. Even when water is present during the evaporation, however, recoveries are often low and erratic and the final technique used is based on the discovery by RUSSELL[2] that a trace of glycerol present with the alkali greatly improves the reproducibility and magnitude of the amount of boron retained after evaporation. The effects of glycerol and water are shown in Tables I and II.

TABLE I

Weight of glycerol *g*	*Quantity of boron* *μg*	*Percentage recovery of boron*
Nil	5	78
Nil	10	83
Nil	15	84
0.07	5	95
0.07	10	96
0.07	15	93
0.14	10	93
0.14	15	94

Volume of liquid 75 ml. Percentage of water 33%. Sodium hydroxide 0.02 g.

TABLE II

Total volume *ml*	*Methanol* *ml*	*Percentage of water*	*Percentage recovery of boron*
250	250	0.5	70
250	200	20	83
250	190	25	84
120	95	20	88
120	90	25	88
120	80	33	94
75	50	33	96
75	50	33	95
75	50	33	94
75	50	33	98
50	45	10	88
25	20	20	93

Sodium hydroxide 0.02 g. Glycerol 0.06 g.

Mannitol has proved to be less satisfactory than glycerol for this purpose. The amount of glycerol is not critical but should exceed 10 mg whilst not being much greater than about 0.1 g. Glycerol interferes seriously with rubrocurcumin or rosocyanin formation and must be removed by volatilisation followed by an ignition of the final traces.

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Typical recoveries of known additions of boron using the optimum conditions of evaporation are included in the tables where it will be seen that a slight loss still occurs. This loss has been found to be nearly constant at 4% and cannot be eliminated by any practicable procedure. For the most accurate work, therefore, a correction of 4% should be added to the determined boron figure.

Method

For Procedure 1 and Procedure 2 (see Part I[1]), collect the methyl alcohol distillate, containing the boron as methyl borate, in a 7.5–9 cm diameter platinum dish containing 2–3 ml of a glycerol–sodium hydroxide reagent, of composition 1% sodium hydroxide, 0.1% sodium chloride and 3% glycerol, and a volume of water equal to at least half that of the alcoholic distillate. It is often convenient (see later), to use for this purpose water already distilled from the sample during the dehydration procedure that is necessary before boric acid esterification takes place.

For Procedure 3 (used with 0.2 µg of boron or less, see Part I) collect the methyl alcohol distillate in a 5 cm diameter platinum dish containing 12 ml of water and 1.0 ml of a glycerol – sodium hydroxide reagent, 0.4% with respect to $NaOH$ and 1% with respect to glycerol.

Determine the boron as described in Part I.

DISTILLATION OF BORON AS METHYL BORATE

General

When less than about 20 µg of boron is to be determined, only silica or platinum-ware can be used throughout the method. Repeated trials of soft-glass or special boron-free glassware have never proved successful in these laboratories, and the susceptibility of such materials to thermal shock would greatly reduce their value under conditions of routine analysis, even if the degree and variability of the contamination introduced by them were at an acceptable level.

The dissolution of samples generally proves to be straightforward and the choice of conditions is related to the distillation procedure finally employed. Boron almost always enters solution as boric acid and losses as boron hydrides have not been substantiated if solutions are either alkaline, or if acid, contain an oxidizing agent. The presence of boron carbide presents a serious problem, unless the sample can be ignited or subjected to an alkaline fusion under oxidizing conditions. Boron in organic materials or carbon products is best concentrated by ignition in platinum rather than by wet-destruction of the sample. The sample should be wetted with a water slurry containing 0.1–0.2 g of calcium hydroxide, dried, and then ignited at below 600°C. The residue, which need not be entirely free from carbon, is then fused in a platinum crucible with 1–2 g of sodium hydroxide to extract the borate. A comparison of recoveries by such a technique and after total combustion in oxygen in a calorimetric bomb has been made and some typical results are shown in Table III.

TABLE III

Sample	*Boron found p.p.m.*	
	After ashing	*After combustion in a calorimetric bomb*
Graphite A	5.50, 5.65	5.5, 5.6
Graphite B	34.5 36.0	37.4, 36.4
Pitch A	4.10	4.05
Pitch B	3.25	3.20
Pitch C	3.45	3.45
Pitch D	3.08	3.15

These results indicate that the ignition procedure is quite satisfactory, although if the boron is organically combined in a particularly volatile state, it would be as well first to check results on such a sample with those obtained by combustion of 0.5–1 g in a bomb.

Apparatus

The apparatus required is essentially simple, consisting of a silica distillation flask and water condenser with preferably a silica dropping funnel fitting into the flask. A soft glass funnel may be used in certain cases when a higher blank can be tolerated. The neck of the flask can be alternatively closed with a stopper. It is highly desirable to avoid the use of cork or rubber, and all joints in this apparatus should be standard ground fittings. The dimensions of the apparatus are not critical but if the flask is too small, spraying into the condenser will be considerable. This can be lessened by having a flask exceeding 200 ml in capacity and taking off the side arm at least 4–5 cm above the bulb. The alternative, the use of a silica plash-head, adds greatly to the cost and has other disadvantages. A suitable apparatus, of general applicability, which can be used for all methods of distillation, is shown in Fig. 1.

Removal of water

In most published methods, the boric acid is esterified in the presence of dehydrating agents such as calcium chloride or sulphuric or phosphoric acids. The simple procedure

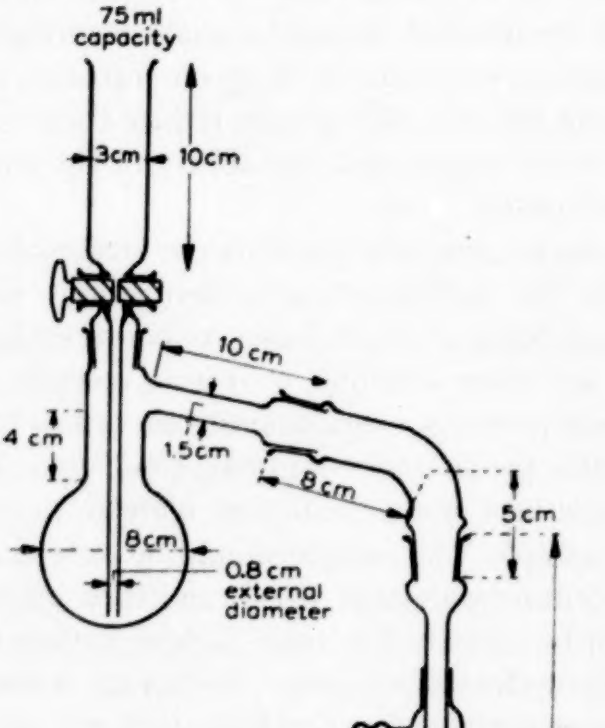

Fig. 1. Scale: approx. 1/3. Standard ground glass joints B 24
The apparatus to be of silica with the exception of the condenser jacket which may be of soft glass.

of removing water by distillation appears to have been avoided because of the possible loss of boric acid by volatilisation in steam. However, when dealing with traces of boron (up to about 20 μg) it has been found that the volatilisation of boric acid is negligible until the volume of water containing it decreases below 2–3 ml. An aqueous solution can be evaporated to this volume, without appreciable loss of boron. The removal of water by distillation is thus practicable and furnishes by far the most simple method of dehydration, although troubles may be encountered when dealing with solutions of easily hydrolysable salts. If a large bulk of salt remains in the flask when the water is distilled, the distillation may often be continued until the salt is quite dry without the loss of boron exceeding a few per cent.

As the presence of a certain amount of water is necessary when evaporating methyl alcohol distillates, it is often convenient to use for this purpose some of the water distilling from the flask. If this water contains the last 5–10 ml distilled, no error whatsoever will arise from the steam distillation of boron and this expedient is to be recommended whenever possible.

An indication of the amounts of water which can be tolerated during distillation of methyl borate will be given when describing the three main distillation procedures.

Effect of acidity

The effect of acidity on the formation and distillation of methyl borate has not been found to be as critical as might be supposed, provided that only a little water is present when the distillation with methyl alcohol takes place. Conditions are no doubt more critical if the alcohol is mixed with much water.

The acidity is most conveniently related to the pH value of the aqueous solution of the substance being analysed *before* the water is distilled off to leave the dry residue for methyl alcohol treatment. This aqueous solution will generally have a volume of between 20 and 100 ml and, provided that pH then lies between about 1.5 and 2, no difficulties should be encountered. Lower pH values are generally impracticable because appreciable amounts of acid distil over with the water and methyl alcohol. At a pH value above 2, the undesirable complication of metallic hydroxide precipitation may be encountered. However, provided that this precipitation does not occur, no appreciable effect on the efficiency of the subsequent esterification and distillation has been noticed with pH values as high as 4 or 5.

Distillation techniques

After suitable dissolution of the sample, conditions for which are too varied for any general principles to be given, the pH is adjusted and water is distilled off to leave a substantially dry residue in the flask. Conditions are chosen, when possible, so that the water distilled is neutral, contains no oxidising agents and is equal in volume to half the volume of methyl alcohol subsequently employed to remove the boron. This water may then be collected directly into a platinum dish containing the glycerol-sodium hydroxide reagent and a drop of thymol blue indicator. The indicator should remain blue during the entire distillation. The boron can then be distilled from the dry residue in the flask by one of three ways, depending on the nature of the solid in the flask. These procedures are outlined below.

The only test of any proposed method at present possible is to measure the recovery of a known quantity of boric acid added to the sample at the commencement of its dissolution. Although complete recovery of the boron should be attempted and is generally possible, a return in excess of 75–80% is often quite adequate when dealing with amounts of boron near to the limits of detection. Generally at least 5 g of sample can be employed and up to 10 g samples of carbon products have been successfully ashed, making the limit of detection ideally of the order of 0.001 parts per million although, in practice, the limitations of contamination control on reagents and apparatus raised the sure limit of detection of a method to the order of 0.01–0.05 parts per million. It is best to resort to the ultra sensitive colorimetric method for determining the distilled boron (see Procedure 3 in Part I) only when a small sample weight is all that is available. Only about 25 ml of alcohol can be accommodated in the small dishes used in this method and any water distilled during the method should be discarded. With this procedure, and any others where the volume of the alcohol distillate becomes too great for the platinum dish used, the last fraction of the distillate may be collected separately in a clean silica or platinum dish and added to the original dish after the alcohol in the latter has been evaporated.

a. Distillation procedure A. This distillation procedure is perhaps the most generally applicable.

It is used with small quantities of materials which are soluble in methyl alcohol (perchlorates, many nitrates, etc.). With large amounts of such salts Distillation procedure C (see below) is more convenient, but the final choice depends largely upon the individual conditions.

The technique consists in treating a residue, of not more than about 5–10 g and which contains no more than 2–3 ml of water, with 35 ml of dry methyl alcohol and distilling at 85°C, later at 95°C, until no more alcohol is removed. The residue is again treated with alcohol (15 ml) and distilled until no more alcohol is removed at 95°C. After this second treatment the contents of the flask should be dry and all the boron will be found in the 50 ml of methyl alcohol distillate.

This method may be varied in detail but consists essentially of one or two distillations with a total volume of 50 ml of methyl alcohol. It has advantages in speed and manipulation over most methods described in the literature. The recovery of boron by this method can be made complete.

The method is best illustrated by its application to the ashes of organic materials. The ash, which should not exceed 0.05 g and which will generally be mixed with 0.1–0.2 g of lime, will have been fused at dull red heat with 1–2 g of sodium hydroxide in a platinum crucible. The melt is extracted with a total of 10–15 ml of water in 3–4 ml portions, warming each time to assist solution. The extracts are poured into the quartz distillation flask and a few drops of an 0.05% solution of thymol blue indicator are added. The solution is neutralised with 2.5*N* perchloric acid until a yellow colour persists and more acid is added to the hot solution until a red colour just fully develops and persists. The excess of perchloric acid should not exceed 2–3 drops, however, or appreciable quantities may distil and give trouble with the curcumin colour development. The volume of the water in the flask is then made to 25 ml and the tap-funnel and condenser are connected. The flask is heated over a burner so that the water distils gently into a platinum dish, containing glycerol and sodium hydroxide, until the volume of the solution has been reduced to 2 ml or until sodium perchlorate begins to crystallize. 35 ml of methyl alcohol are then added from the funnel and distilled from a water bath until distillation ceases and the residue further treated with a 15 ml portion of alcohol, after which it should go completely dry. The end of the condenser should always be just below the level of liquid in the platinum dish throughout the alcoholic distillations.

Typical results by *Distillation procedure A* are shown in Table IV.

TABLE IV

2.5 M sodium perchlorate in distillation flask

Boron added to flask µg	*Percentage of boron recovered in 50 ml of methanol distillate*
5	96
5	102
5	100
10	99
10	95
10	97
10	96
15	98
15	97
15	91
Mean	97

Ten determinations at 10 µg level gave mean of 96.1% and standard deviation of 0.18 µg.

It will be seen that the mean recovery is the same as that from synthetic distillates showing that quantitative distillation takes place.

b. Distillation procedure B. The technique outlined above can often be successfully applied to substances which are not freely soluble in alcohol. It seems reasonable to assume, therefore, that on recrystallisation from water, boric acid is left largely on or near the surface of most solid residues.

Practical considerations ("bumping" during distillation, etc.) restrict the amount of material that can be treated in this manner, the quantity generally being less than with Procedure A. It is also normally necessary to redissolve in a little water the solid remaining after the first treatment with methyl alcohol, again evaporating the solution to dryness. Treatment of this recrystallised residue with a further quantity of alcohol (for example the 15 ml addition recommended in Procedure A) then completes the separation of all the boric acid, a little of which does not always react during the treatment of the first residue with methyl alcohol.

The determination of boron in many insoluble salts has been made in this way. The amount of water which can be tolerated is similar to the amount permissible with Procedure A, but recoveries are sometimes not quite so satisfactory, although for practical purposes adequate (85–90%).

This method may be illustrated by its application to the determination of boron in a salt such as barium chloride. 10 g of barium chloride dihydrate is added to the quartz distillation flask and dissolved in 35 ml of water. A little methyl red indicator is added followed by 1 *N* hydrochloric acid until the red colour is just fully developed. The tap funnel and condenser are connected to the flask which is surrounded by a glycerol bath at 125°C and the contents distilled until apparently dry. Finally the glycerol bath is raised in temperature to 140°C until the residue in the flask is quite dry and light in colour. The distillate is collected in a platinum dish containing glycerol–sodium hydroxide and when cooling the flask, the tap funnel should be opened to prevent suck-back. 35 ml of methyl alcohol are then distilled from the residue, as in Procedure A above, and then a further 15 ml of water is introduced from the tap funnel and allowed to redissolve the barium chloride. This water is distilled and the residue treated with a further 15 ml of alcohol. The boron is determined in the combined aqueous and alcoholic distillates.

Typical results by *Distillation procedure B* are shown in Table V.

TABLE V

Salt in distillation flask	*Boron added µg*	*Boron in first distillate (35 ml) µg*	*Salt redissolved in water*	*Boron in second distillate (15 ml) µg*	*Percentage of boron recovery for combined distillates*
10 g	10	9.0	Yes	1.0	100
$(NH_4)_2SO_4$	10	8.3	Yes	1.2	95
2 g	5	—	No	—	94
Na_2SO_4	10	—	No	—	98
	15	—	No	—	97
10 g	10	—	Yes	—	91
$BaCl_2.2H_2O$	10	—	Yes	—	95
	10	—	Yes	—	94
				Mean	95

Again, the mean recovery indicates complete recovery of the boron.

c. Distillation procedure C. The third general method is used with methyl alcohol soluble materials where the bulk of material is too large to make it practicable to distil the water or alcohol to complete dryness. The technique consists of distilling methyl alcohol through an alcoholic solution of the material under examination, the rate of distillation and the addition of alcohol being adjusted so that the volume of liquid in the flask remains constant (about 50 ml). The methyl alcohol is introduced as liquid, by means of the funnel fitting in the neck of the distillation flask with its stem reaching to the bottom of the flask. Such a procedure requires the minimum of manipulative skill and although complete recovery is theoretically impossible, an undetectably small amount of boron will remain after sufficient distillation, and the recovery may, in practice, be considered to be complete.

As with Procedure A, the substance under examination must have most of the water removed from it prior to distillation with alcohol, or an undesirably large volume of the latter will be required for complete separation of the boron. No general statement of the maximum permissible volume of water can be made, as this varies with the material and with the volume of alcohol which is passed through the flask, the passage of methyl alcohol having a definite dehydrating effect. In general, the volume of water should not exceed 2–3 ml but often as much as 10 ml can be tolerated.

The best procedure when investigating the use of this technique with any new set of conditions, is first to remove as much water as is practicable (in no case leaving more than about 10 ml including the water of crystallisation of any salt) and then dissolve the residue in 50 ml of methyl alcohol. On passing 20–30 ml volumes of alcohol through this solution and determining the boron separately in each distillate, the minimum volume of alcohol required for complete recovery of the boron can be determined. Provided that this volume is under 100 ml (preferably under 75 ml), the method may be considered to be satisfactory.

The fraction f of the total boron which distills in a volume v ml of alcohol, with the volume of alcohol in the flask, V, being held substantially constant, is given by an expression of the form:

$$f = 1 - \exp\left(- k.\frac{v}{V}\right)$$

In favourable cases the constant k exceeds 3 and the volume of distillate need not exceed the volume of alcohol in the flask.

To illustrate the method, an outline will be given of the determination of boron in calcium metal after a preliminary dissolution of the sample in hydrochloric acid. 7 g of sample are added in small portions to 50 ml $8N$ hydrochloric acid in a distillation flask, immersed in ice-water to control the reaction. When solution is complete, the liquid is made alkaline to methyl red by the addition of calcium hydroxide suspension and then just acid with $2N$ hydrochloric acid. The tap funnel and condenser are connected to the flask and the contents gently boiled to distil off the water. When the volume is reduced to about half, the flask is heated in an oil bath and the temperature raised gradually to 220°C until water ceases to distil. The distillate is rejected.

After cooling, the condenser is dipped below the surface of 25 ml of water in a 9 cm diameter platinum dish containing 2 ml glycerol sodium hydroxide and thymol blue indicator. 50 ml of methyl alcohol are added to the flask which is warmed to assist solution of the calcium chloride and then heated in a water bath at 85°C. The level of the solution in the flask is noted by marking the outside and a total of 50 ml of methyl alcohol are added, a little at a time, so as to keep the level in the flask approximately constant. After each addition, the contents of the flask should be swirled gently to ensure mixing. Boron is determined on the distillate. Recoveries of 94–98% have been obtained from added quantities of boron varying between 1 and 10 μg.

PRECAUTIONS NECESSARY TO MINIMIZE CONTAMINATION DURING THE DETERMINATION OF BORON

Purification of reagents

Experience has shown that some purification is nearly always necessary even with reagents of analytical purity. An outline will be given of the methods used to minimize the contamination introduced from the more common chemicals used in boron determinations.

Water. Tap water contains boron of the order of 0.01–0.5 p.p.m. and is unsuitable. Some distilled water may have as much as 0.003 p.p.m. of boron present or may have been contaminated and, for safety, it is desirable to redistil the water before use. This should be done in a tin lined apparatus with a trace of mannitol (approx. 0.1 g/l of water) in the boiler. The redistilled water should then contain less than 0.001 p.p.m. of boron and contribute no recordable blank.

Methyl alcohol. Supplies of anhydrous methyl alcohol may contain a trace of boron but this is likely to be small (0.002 p.p.m.). In view of the possibility of variation in boron content and contamination, however, it is best to distil the alcohol before use from lime in a soft glass or metal apparatus. A suitable procedure is to distil 2–3 l at a time over 200-300 g of good quality calcium oxide. The first 200 ml distilling are rejected, approximately three quarters of the remainder collected and the lime and residual alcohol removed from the flask before the next distillation. If a boro-silicate glass flask is used, no contamination results provided several grams of sodium hydroxide are added as well as the lime. The resulting distillate is dry and absolutely safe for use, giving no appreciable blank contribution. It may be stored for many weeks in soft glass.

Sodium hydroxide. Analytical reagent grade pellets are the most suitable form and normally give a little or no blank. If pellet or stick-form caustic soda is suspected of surface contamination, it should be rinsed in a solution containing 1 part of methanol and 2 parts of water, and dried in a platinum dish before use.

Ammonia solutions. The boron content of analytical reagent quality aqueous ammonia does not exceed 0.01 p.p.m. Should purification be necessary, the gas should be evolved by heating and collected in redistilled water. This distillation must be made in an all silica apparatus.

Calcium hydroxide. This is best prepared by treating the high purity metal with water.

Perchloric acid. This reagent is very useful as most of its salts are soluble in methyl alcohol but unfortunately the boron content of even the analytical quality material may be relatively high (about 0.05 p.p.m.). Perchloric acid of other than analytical quality has never been found to be satisfactory and the boron content of even the latter varies widely. No really satisfactory method of purification is known but the boron content can be reduced to about half if the acid ("60" or "70%") is treated with a tenth of its volume of "40%" hydrofluoric acid and evaporated to fumes.

Nitric acid. The analytical reagent material is normally satisfactory for use, containing about 0.005 p.p.m. of boron, but if purification is desirable, this can be achieved by distillation (rejecting the first and last 10%).

Hydrochloric acid. Analytical reagent quality material is normally satisfactory for use, containing less than 0.01 p.p.m. of boron. If purification is necessary, this can only be achieved by boiling the concentrated acid and collecting the hydrogen chloride evolved in water.

Storage of solutions

For neutral or acid solutions ordinary soft-glass vessels, provided that they are thoroughly cleaned before use with concentrated hydrochloric acid, methyl alcohol and finally water, have been found to be satisfactory. Alkaline solutions, such as the glycerol-sodium hydroxide reagents, must be kept in stoppered silica flasks.

When it is necessary to store methyl alcohol distillates over night in platinum dishes, they should be protected by a silica cover or placed under a large clean glass beaker. It is imperative, however, that if glass is used near alcoholic distillates, no hydrofluoric acid vapour is in the vicinity. Contamination by many tens of μg of boron was recorded when glass covered distillates were placed overnight in a fume-cupboard containing crucibles that still retained a small amount of hydrofluoric acid.

Apparatus contamination

When commencing with new silica distillation apparatus it must be cleaned by boiling it in concentrated hydrochloric acid and then several hundred ml of slightly acidified methyl alcohol should be distilled through the apparatus until 50 ml of distillate contains less than 0.1 μg of boron.

There is evidence that when boron is distilled from a sample, some 0.5-1% of the boron is retained on the surfaces of the apparatus and cannot be removed by rinsing with water or alcohol. This behaviour causes no appreciable error if the same magnitude of boron is always being distilled from the same apparatus but should a relatively large amount of boron, say over ten times the normal, be accidently introduced into the flask and distilled, serious contamination of the following determination may result. When this occurs, the apparatus must be re-cleaned by the repeated distillation of acidified methyl alcohol. The effect is most serious when quantities of boron under 1-2 μg are being determined and it is essential that any silica apparatus habitually used for such amounts be retained specifically for this purpose.

The bulk of the boron in platinum dishes is converted to rosocyanin or rubrocurcumin, and hence removed when the dishes are extracted with alcohol prior to extinction measurements, but with Procedures 1 and 2, described in the previous paper, some uncombined boric acid may remain. For safety, therefore, all dishes should be thoroughly rinsed with water after use.

The only other serious cause of contamination from apparatus that has been encountered is from the lining of those muffle furnaces which contain borate deliberately added to the ceramic. Some linings may contain up to 5% of boric oxide. When organic matter is ignited in such a muffle, the vapour pressure of boric oxide is sufficiently high even at 600°C, for µg amounts of boron to be transferred to alkali residues in the platinum dishes. This type of furnace lining is not common but the possibility should be checked before a new type of furnace is put into use.

Other sources of contamination

With a close control on the purity of reagents and apparatus, no other difficulties should be encountered except for air-borne contamination from dust. This can be appreciable as a laboratory dust in industrial areas may contain as much as 200–1000 p.p.m. of boron. Samples or ashes should be stored in a desiccator if kept for any length of time and the water bath used for the evaporation of distillates should have a sheet of glass or plastic suspended some 30–50 cm above it.

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The work here described, which was carried out in the laboratories of the Chemical Inspectorate, Ministry of Supply, when the authors were members of the staff of that Inspectorate, formed part of a programme extending over many years and resulted from the co-operation of many workers with the authors. It is wished to acknowledge, in particular, the assistance of Miss K. ALLAN, Messrs. E. BOWELL, R. W. CRIPPS, W. FURNESS, A. H. HOLLOWAY, Miss J. STRACHAN and Mr. A. H. WRIGHT.

SUMMARY

Methyl alcohol distillates containing µg amounts of boron may be evaporated without loss of boron by first adding water, sodium hydroxide and glycerol. The resulting residues can be used directly in the curcumin absorptiometric methods previously described. The distillation techniques developed over the last decade by the United Kingdom Atomic Energy authority are briefly described, as these can be used for the separation of boron from practically all types of sample, including organic matter after it has been ashed with lime. In all cases aqueous solutions of the samples are made slightly acid (pH 1.5–5) and evaporated nearly to dryness. Residues are then treated with methyl alcohol in one of three ways according to their properties. It is essential to use all-silica distillation apparatus and platinum dishes for collecting distillates. Notes are given of other precautions necessary to minimize contamination from reagents and other sources. The methods are rapid and suitable for routine analysis on up to 10 g of sample. Under favourable conditions, the limit of detection is of the order of 0.01 p.p.m. of boron. A precision of better than 5% can be obtained with amounts exceeding about 0.2 p.p.m.

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A RAPID AND PRECISE MICROHETEROMETRIC DETERMINATION OF MERCURY WITH *p*-DIMETHYLAMINO-BENZYLIDENE-RHODANINE

by

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INTRODUCTION

A heterometric method for the determination of traces of mercuric mercury with *p*-dimethylamino-benzylidene-rhodanine (= DBR) in aqueous solutions of any foreign metal without previous separation is presented here. In all cases the amount of mercury was less than one-half of a per cent of the total metal content. 0.1 mg of mercury in 20 ml of solution was sufficient for the determination which took 4-6 min at room temperature. The error was, in general, negligible; in exceptional cases it amounted to about 1%. Mercury was determined successfully in the presence of Ca, Ba, Mg, Zn, Mn, Ni, Co, Al, Cr(III), Fe(III), Cd, Cu, Pb, U(VI), Tl, Th, Ce(III), Sb(III) and Bi(III). Special consideration was given to the determination of mercury in the presence of Au(III), Pt(VI), Pd(II) and Ag.

EXPERIMENTAL

A 0.002*M* DBR stock solution in acetone was prepared. This solution was then diluted approximately six times with ethyl alcohol. More dilute solutions were prepared by diluting this solution with alcohol. Alcohol was used because of its higher boiling point. The solutions were stable for a very long period. The DBR was a Hopkin and Williams spot test reagent. The other chemicals were all either AnalaR or chemically pure reagents. The working conditions were the same as in previous heterometric work[1].

All titrations with DBR were carried out using a Fisher (= Corning) green filter (525) generally supplied with the Fisher Electrophotometer which gives maximum transmission at 525 mμ. This filter was the most suitable for the determinations with DBR.

RESULTS AND DISCUSSION

A selection of experiments carried out and the results obtained are given in Tables I and II and in Figs. 1 and 2. Table I contains titrations of mercury mostly carried out in the presence of other metals. Expts. 1-5 were carried out in the absence of foreign metals.

Titrating conditions

From previous investigations[2] it was known that heterometric titrations with DBR can be successfully carried out either in neutral or in basic solution. In acid solutions the DBR is itself precipitated and the determination becomes impossible in many cases. In solutions containing borax or ammonia (pH ∼ 10) no precipitation of mercury occurred, (Expt. 4). In the presence of excess citrate or tartrate the titration of mercury was normal and the end-point corresponded to the quantitative formation of $Hg(DBR)_2$ after which a horizontal maximum line was obtained. As may be seen from curve 1,

TABLE I

Content Hg: 0.1003 mg; concentration Hg: $2.5 \cdot 10^{-5}M$; T = 20°; filter: Fisher green filter (525).
Composition: 5 ml 0.0001*M* $Hg(NO_3)_2$ + *b* ml supplements + (15—*b*) ml H_2O + *x* ml *cM* DBR (= *p*-dimethylamino-benzylidene-rhodanine) (alc.).

Expt. No.	Supplements	% Hg	Molarity of DBR	Found: ml DBR	Found: Maximum density value	Found: Titration time in min	Found: % error	Remarks
1	5 ml *M* Na_3-citrate		0.00025	i 3.95 h	0.59	5	1.0	Another intersection point at 2.90 ml DBR = 2[Hg]: 3[DBR] *D* = 0.53.
2	5 ,, ,, ,, + 2 ml 0.5*M* Na_2HPO_4		0.00025	i 2.96 h	0.52	4	1.3	End-point at 2[Hg]: 3[DBR]
3	5 ,, ,, Na_2-tartrate + 2 ,, 0.5*M* Na_2HPO_4		0.00025	i 3.00 h	0.50	4	0.0	End-point at 2[Hg]: 3[DBR]
4	5 ,, ,, Na_3-citrate + 10 ,, 0.1*M* $Na_4B_2O_7$							A clear yellow solution.
5	5 ,, ,, ,, + 1 ,, 0.1*M* KCN							Low density.
6	5 ,, ,, ,, + 1 ,, 2*M* $Ca(NO_3)_2$	0.1	0.00025	i 3.94 h	0.64	5	1.5	
7	5 ,, ,, ,, + 1 ,, *M* $Ba(NO_3)_2$	0.07	0.00033	i 3.00 h	0.70	4	0.0	
8	5 ,, ,, ,, + 2 ,, *M* $Mg(NO_3)_2$	0.2	0.00025	i 4.00 h	0.75	8	0.0	
9	5 ,, ,, ,, + 1 ,, *M* $Zn(NO_3)_2$	0.15	0.00025	i 4.00 h	0.73	5	0.0	
10	5 ,, ,, ,, + 1 ,, *M* $MnSO_4$	0.2	0.00025	i 4.00 h	0.73	6	0.0	
11	5 ,, ,, ,, + 1 ,, *M* $Ni(NO_3)_2$	0.15	0.00025	i 3.98 h	0.75	4	0.5	
12	5 ,, ,, ,, + 2 ,, *M* $Co(NO_3)_2$	0.07	0.00025	i 3.96 h	0.40	5	1.2	
13	5 ,, ,, ,, + 1 ,, *M* $Al(NO_3)_3$	0.4	0.00025	i 3.99 h	0.78	4	0.2	
14	5 ,, ,, ,, + 0.5 ,, *M* $Cr(NO_3)_3$	0.4	0.00025		0.85	5		Short horizontal max. line then increase.
15	5 ,, ,, ,, + 0.3 ,, *M* $Cr(NO_3)_3$	0.5	0.00025	i 3.99 h	0.72	5	0.2	
16	5 ,, ,, ,, + 0.5 ,, *M* $FeCl_3$	0.4	0.00025	i 3.98 h	0.70	4	0.5	
17	5 ,, ,, ,, + 1 ,, 0.5*M* $Cd(NO_3)_2$	0.2	0.00025	i 4.00 h	0.75	5	0.0	
18	5 ,, ,, ,, + 1 ,, 0.5*M* $CuSO_4$	0.3	0.00025	i 4.00 h	0.63	5	0.0	
19	5 ,, ,, ,, + 1 ,, *M* $Pb(NO_3)_2$	0.05	0.00025	i 4.00 h	0.72	5	0.0	
20	5 ,, ,, ,, + 5 ,, 0.2*M* $UO_2(NO_3)_2$ (add 30 ml H_2O)	0.04	0.00033	3.02	0.81		0.7	After the break a linear increase of density.
21	5 ,, ,, ,, + 1 ,, 0.2*M* $UO_2(NO_3)_2$	0.2	0.00025	i 4.00 h	0.72	4	0.0	
22	5 ,, ,, ,, + 5 ,, 0.1*M* $Tl(NO_3)_2$	0.1	0.00025	i 4.00 h	0.74	4	0.0	
23	5 ,, ,, ,, + 2 ,, 0.1*M* $Th(NO_3)_4$	0.2	0.00025	i 4.00 h	0.73	5	0.0	
24	5 ,, ,, ,, + 2 ,, 0.1*M* $ZrO(NO_3)_2$	0.5	0.00025	i 4.00 h	0.72	5	0.0	
25	5 ,, ,, ,, + 2 ,, 0.1*M* $Ce(NO_3)_4$	0.4	0.00025	i 3.98 h	0.76	4	0.5	
26	5 ,, ,, ,, + 1 ,, *M* $SbCl_3$ (2*N* HCl) + 2 ml 0.5*M* Na_2CO_3	0.07	0.00025	i 4.00 h	0.71	4	0.0	
27	5 ,, ,, ,, + 1 ,, *M* $Bi(NO_3)_3$ (3*N* HNO_3) + 3 ml 0.5*M* Na_2CO_3	0.04	0.00025	i 4.01 h	0.71	5	0.2	

i = intersection; h = horizontal maximum density line.

TABLE II

Titration time: 4–6 min; T = 20°; filter: Fisher green filter (525).

Composition: *a* ml $Hg(NO_3)_2$ + *b* ml other metal + *c* ml supplements + (20—*a*—*b*—*c*) ml H_2O + *x* ml 0.00025*M* DBR (= *p*-dimethylamino-benzylidene-rhodanine).

Expt. No.	*Hg(NO₃)₂*		*Other metal*			*Supplements*	*mg*		*Hg %*	*DBR used*				*% error*	
										at 1st point		*at 2nd point*			
	ml	*molarity*	*name*	*molarity*	*ml*		*Hg*	*other metal*		*ml*	*density*	*ml*	*density*	*at 1st point*	*at 2nd point*
28	5	0.0001	$H[AuCl_4]$	0.001	1	5 ml *M* Na_3-citrate	0.1003	0.1972	33.8	i 4.00 h	0.77	—	—	0.0	
29	5	0.0001	,,	0.001	2	5 ,, ,, ,,	0.1003	0.3944	20.3	i 4.01 h	0.90	—	—	0.2	
30	5	0.0001	,,	0.001	3	5 ,, ,, ,,	0.1003	0.5916	14.5	i 4.00 h	0.99	—	—	0.0	
31	5	0.0001	,,	0.01	2	1 ,, ,, ,, + 1 ml 0.1*M* dimethylglyoxime (alc.)	0.1003	3.944	2.5	i 4.00 h	0.47	—	—	0.0	
32	5	0.0001	$H_2[PtCl_6]$	0.004	1	5 ,, ,, Na_3-citrate	0.1003	0.7809	11.4	i 4.00 h	0.76	—	—	0.0	
33	5	0.0001	,,	0.004	2	5 ,, ,, ,,	0.1003	1.5618	6.0	i 4.00 h	0.74	—	—	0.0	
34	5	0.0001	$PdCl_2$	0.0002	2	5 ,, ,, ,,	0.1003	0.0427	70.0	i 4.00 h	0.71	—	—	0.0	
35	5	0.0001	,,	0.0002	3	5 ,, ,, ,,	0.1003	0.0640	61.0	i 4.00 +	0.75	—	—	0.0	
36	5	0.0001	,,	0.0002	5	5 ,, ,, ,, + 0.5 ml 0.1*M* dimethylglyoxime	0.1003	0.1067	48.5	i 4.00 +	0.73	—	—		
37	4	0.00005	$AgNO_3$	0.0001	6	5 ,, ,, ,,	0.0401	0.06473	38.3	i 2.46(Ag)	0.58	i 4.00 h	0.67	2.0	0.0
38	3	0.00005	,,	0.0001	6	5 ,, ,, ,,	0.0301	0.06473	31.8	i 2.36(Ag)	0.53	i 3.57 h	0.60	2.0	1.0
39	6	0.00005	,,	0.0001	4	5 ,, ,, ,,	0.0602	0.04315	58.3	i 2.40(Hg)	0.55	i 3.98 h	0.62	0.0	0.5

i = intersection; h = horizontal maximum density line; + = short horizontal line then increase of density.

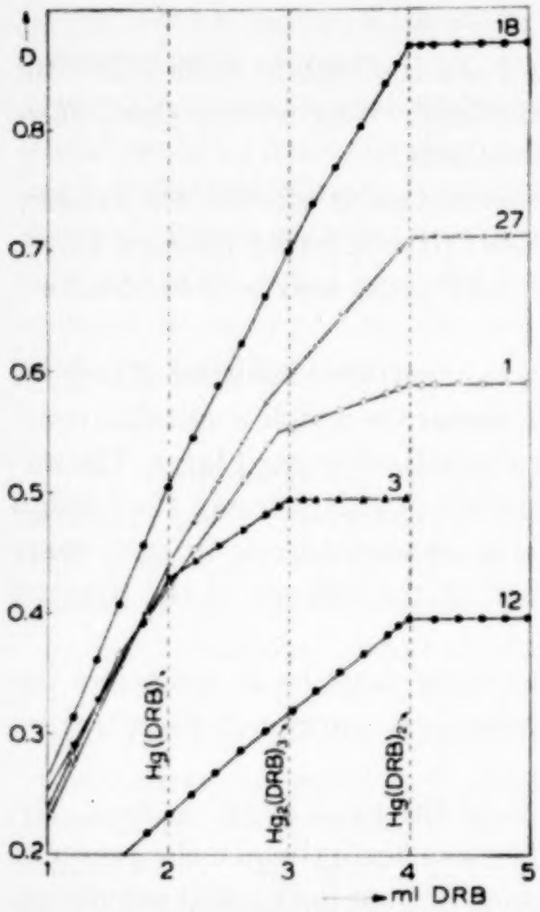

Fig. 1. Titration of mercuric nitrate with *p*-dimethylamino-benzylidene-rhodanine.

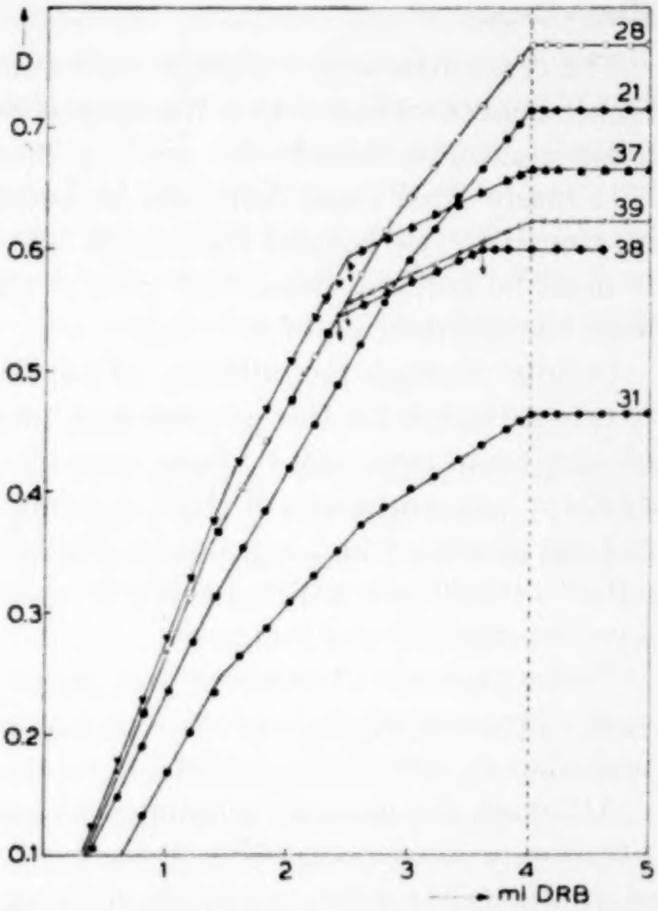

Fig. 2. Titration of mercuric nitrate with *p*-dimethylamino-benzylidyne-rhodanine in the presence of gold, platinum, palladium or silver.

another intersection point (= "critical point") was also obtained at the approximate molar ration of 2 Hg : 3 DBR. Since the entire titration only lasted 5 min, the transformation of the intermediate $Hg_2(DBR)_3$ into the final compound $Hg(DBR)_2$ occurred very rapidly in spite of the fact that the reaction evidently took place in a heterogeneous system.

It is very interesting to note that when the titrations were carried out at pH$\sim$9 (= Na_2HPO_4) in the presence of tartrate *two* critical points were obtained, the first one at the molar ratio of 1 Hg : 1 DBR and the second, which coincided with the first maximum density point, at the molar ratio of 2 Hg : 3 DBR. After this point a horizontal maximum line was obtained (curve 3). The maximum density value also appeared to be somewhat lower in these solutions. The maximum point at $Hg_2(DBR)_3$ can, therefore, also be used for the heterometric determination of mercury.

From Table I, it can also be seen that the maximum density values achieved were somewhat higher in the presence of foreign salts than in their absence. In all these cases the specific influence of the Fisher filter (525) was responsible for the high density values obtained. No other Corning filter showed such a favourable effect. Probably the densities measured were only partly caused by the precipitate as there is a combined effect caused by the precipitate *and* the solution simultaneously. The influence of the filter is evident when comparing the high maximum density values which were generally obtained with the maximum density value measured in the presence of cobalt nitrate (Expt. 12). Evidently the light absorption of the cobalt solution reduces the favourable effect of the Fisher filter.

Foreign salts

The concentrations of foreign salts cited in Table I are the highest tolerable. Still higher concentrations cause the optical density to continue rising after a short *horizontal* maximum density line with further addition of DBR.

In many other cases there was no horizontal maximum line at all, but the density continued to rise beyond the calculated end-point, the curve altering its slope there. It must be borne in mind that even in this case, the end-point may still be obtained from the intersection of two lines.

In order to mask the influence of the foreign salt, a concentrated solution of sodium citrate sufficient for this purpose was used. The only metal for which a suitable complexing agent could not be found was silver. This case will be discussed later. The addition of larger amounts of DBR in alcohol, resulted in the precipitation of the foreign salt (see Expts. 7 and 20), not by the DBR but by the alcohol added. In such cases either a more concentrated solution of DBR was used or the volume of the titrated aqueous solution was increased.

In the presence of *antimony* and *bismuth*, sodium citrate must be added *before* the *acid* solution is neutralized with carbonate. It is advisable to carry out the titration immediately afterwards whilst the solution is clear.

Although the mercury amounted to less than 0.1% of the total metal content, the titration proceeded smoothly in all cases, and the error was negligible. In the presence of *uranium*(VI), when the latter made up more than 99.9% no horizontal maximum density line was obtained (Expt. 20), but when it amounted to 99.8%, a regular horizontal maximum density line was obtained, and the error was small (Expt. 21). As Table I shows, the error was in very many cases nearly zero and only in exceptional cases did it amount to 1% or more.

Foreign noble metals

A selection of titrations carried out in the presence of gold, platinum, palladium and silver is compiled in Table II. A concentrated solution of trisodium citrate, which sometimes contained dimethylglyoxime as well, was used as a complexing agent. With gold chloride present in the citrate solution the mercury only amounted to 15% (Expt. 30). When dimethylglyoxime was added to the gold solution the titration was successful although the amount of mercury was only 2.5%. An intense blue solution was obtained before commencing the titration. It was advisable to carry out the titration immediately after the addition of dimethylglyoxime, otherwise it took another course. The error was generally small (Expts. 28-30).

In the presence of chloroplatinic acid the titration of mercury was successful even when the platinum amounted to 90% of the total (Expts. 32 and 33). Only limited amounts of *palladous chloride* could be present in solution (Expts. 34-36).

Presence of silver

In a previous investigation[2] a method for the determination of traces of silver in excess of mercury with DBR was presented. On the other hand, no masking agent could be found which would make the determination of mercury in the presence of silver possible: the silver was always precipitated together with the mercury. Therefore an attempt was made to determine the sum of both metals when their amounts (Expts.

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37-39) were roughly of the same order of magnitude. Generally the sum could be determined with an error of 1% or less. The curves obtained (see Fig. 2) were especially interesting because each possessed *two* critical points from which the amount of each metal could be determined separately. The *first* critical point always gave the amount of the metal which made up more than about 50% of the total metal content. The second point coincided with the first maximum density point after which a horizontal density line was obtained. This point gave the *sum* of both metals. Although the first point showed an error of 2%, there is no doubt that with some experience better results could be achieved.

SOLUBILITY OF THE COMPOUNDS

The compounds $\mathrm{Hg(DBR)_2}$, $\mathrm{Hg_2(DBR)_3}$ and $\mathrm{Hg_1(DBR)_1}$, were prepared in larger amounts under conditions similar to those of Expts. 1 and 2. The suspensions obtained were centrifuged and small portions of the precipitates ware tested for solubility in the following organic solvents:

methyl alcohol, ethyl alcohol, diethyl ether,
dioxane, chloroform and carbon tetrachloride.

It was found that the three compounds mentioned above behaved similarly with respect to any particular solvent. If one was insoluble, all were insoluble and vice versa. They were all soluble in methyl alcohol giving brownish solutions. In *dioxane* they dissolved immediately; $\mathrm{Hg_1(DBR)_1}$ gave a greenish yellow solution while the other compounds gave pure yellow colorations. They also dissolved in *chloroform* giving yellow solutions, but were scarcely soluble in *ethyl alcohol* and insoluble in *carbon tetrachloride*.

DETERMINATION OF MERCURY

The determination is best carried out in a *neutral* solution in the presence of excess trisodium citrate. As little as 0.1 mg mercury in 20 ml solution can be determined in about 5 min. The end-point coincides with the first maximum density point and is always at the point corresponding to quantitative formation of $\mathrm{Hg(DBR)_2}$. When the titration is carried out in *basic* citrate solution, phosphate must be used as buffer (pH $\sim$ 9), since in the presence of ammonia no precipitation occurs. The maximum density value obtained in this case (pH $\sim$ 9) is somewhat lower than at pH $\sim$ 7.

The compound formed is $\mathrm{Hg_2(DBR)_3}$.

In the presence of silver

When mixtures of mercury and silver are to be titrated there are *two* possibilities for the determination.

1. When both metals are present in amounts of the same magnitude, they can be determined in *one* titration only at pH $\sim$ 7 in citrate solution. The curve obtained has *two* critical points, the first giving the amount of the metal which constitutes more than 50% of the total metal content. The second and final critical point gives the exact sum of both metals ($= \mathrm{Hg(DBR)_2} + \mathrm{Ag(DBR)}\downarrow\downarrow$).
2. Another method may be chosen when the solution contains mercury in considerable excess. The mercury is held in solution with excess EDTA and ammonia and only the silver is determined. In a second titration in citrate solution at pH $\sim$ 7, the sum of both metals is determined as before.

All the above titrations are carried out using the Fisher (= Corning) green filter (525) which has a maximum transmission at 525 mμ.

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General method

20 ml of a solution containing ∼0.1 mg mercury and about 5 ml M trisodium citrate is titrated at pH ∼ 7 with 0.0025M *p*-dimethylamino-benzylidene-rhodanine.

SUMMARY

1. In citrate or tartrate solutions mercury formed three different compounds with *p*-dimethylamino-benzylidene-rhodanine at pH ∼5, ∼7 and ∼9. The composition of the compounds is discussed.

2. Analytical methods are presented for the determination of 0.1 mg mercury in 20 ml solution which contained 99.5–99.9% foreign metals. In most cases the error lay between zero and 1%. The foreign metals were: Ca, Ba, Mg, Zn, Mn, Ni, Co, Al, Cr(III), Fe(III), Cd, Cu, Pb, U(VI), Tl(I), Th, Ce(III), Sb(III) and Bi(III). Methods for the determination of 0.1 mg mercury in gold(III), Pt(VI), Pd(II) and silver are also presented.

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DETERMINATION OF BIPHENYL IN THE PRESENCE OF POLYPHENYLS

WATER SOLUBILITY METHOD*

by

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Biphenyl, the lowest member in the polyphenyl series, is one of the more heat stable organic compounds. Along with biphenyl oxide, it is used in industry as a heat transfer medium, under the name of Dowtherm. The three isomeric terphenyls and the higher polyphenyls are expected to be carefully investigated in the future, some in combination with biphenyl as heat transfer media.

Preliminary pyrolysis experiments on *p*-terphenyl indicated that one of the by-products is biphenyl and that higher polymers[1] are to be expected when polyphenyls are heated over long periods of time. The determination of small amounts of biphenyl in the presence of large amounts of *p*-terphenyl and associated polyphenyls was the object of this research.

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* This report is based on studies conducted for the Atomic Energy Commission under Contract AT-11-1-GEN-8.

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BOHON AND CLAUSSEN[2] studied the solubility of benzene, biphenyl, naphthalene, and other hydrocarbons in water. The evaluation of the solubility of biphenyl was made either by determining the absorbance of the water solution or by extracting[3] the water solution of biphenyl with an organic solvent before determining the absorbance. ANDREWS AND KEEFER[3] found the solubility of biphenyl in water to be 5.94 mg/l at 25°C, while BOHON AND CLAUSSEN's figure is 7.48 mg/l at the same temperature.

Our solubility data point toward a still higher value. Since the solubility is a saturation figure, the experiments described in this paper were usually aimed toward a 50% saturated solution (about 4 mg biphenyl/l of water). Since the rate of solubility is low[2], studies on the effects of mixed solvents and temperature of the water solvent were included. Expected interferences by the other polyphenyls were also checked.

Methods other than the solubility and distillation methods for the separation of biphenyl from the other polyphenyls were not examined. The method of MORRIS, STILES AND LANE[4] is of use for spot tests for certain polyphenyls as well as is the later method described by SILVERMAN AND BRADSHAW[5].

PROCEDURE

Prepare the standard curve by weighing 0.01 to 1.2 mg portions of finely ground biphenyl into 500-ml volumetric flasks. Make up to volume with distilled water and seal the glass stopper with tape. Place the flask in a 55°C oven for 40 h or in a temperature-controlled water bath for 24 h. Shake the flask frequently. Cool and obtain the absorbance readings on a Beckman DU spectrophotometer at 247 to 250 mμ, using water as a reference solution.

EXPERIMENTAL RESULTS

Spectrophotometric curves

BOHON AND CLAUSSEN[2] noted that the wave length of maximum absorption for biphenyl moves toward lower wave lengths as the solvent changes from hydrocarbon (heptane or cyclohexane) to alcohol to water. In addition[1] there is a slight shift in the wave length of maximum absorption as the concentration of the solute increases. For these reasons, in this paper, the absorbance reading is the maximum reading obtained in the 247 to 250 mμ range.

The first points to be determined are: conformance of the biphenyl solute in aqueous solution to Beer's law, similarity of absorbance in water to that in cyclohexane[1], and the limit of solubility of biphenyl in water.

These were determined by dissolving weighed amounts of biphenyl in water at 55°C, up to and beyond the saturation point (Fig. 1).

Fig. 2 shows a family of spectrophotometric curves for the solution of biphenyl in water. These curves may be superimposed approximately on those for biphenyl in cyclohexane[1], and are found to follow Beer's law at wave lengths such as 216, 222, 230, 250, and 260 mμ. In cyclohexane, the plots are linear up to a concentration of about 2.4 mg/l[1].

Having found that the spectrophotometric curves for biphenyl in water and in cyclohexane are nearly coincident, the curves in Fig. 1 are then useful in showing that the solubility of biphenyl in water is about 0.8 mg/100 ml, similar to the value found by BOHON AND CLAUSSEN[2], but higher than that of ANDREWS AND KEEFER[3], and further, that a supersaturated solution (1.2 mg/100 ml) may also be produced.

The purpose of determining the maximum solubility (and supersaturation) of biphenyl in water is not to corroborate existing values, but rather to establish a practical

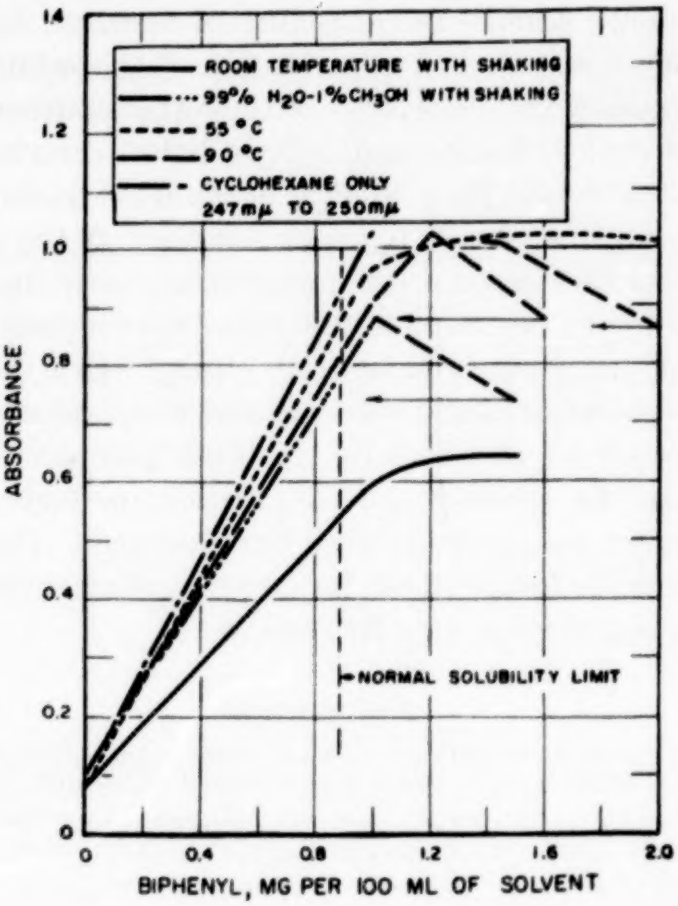

Fig. 1. Solubility of biphenyl in water.

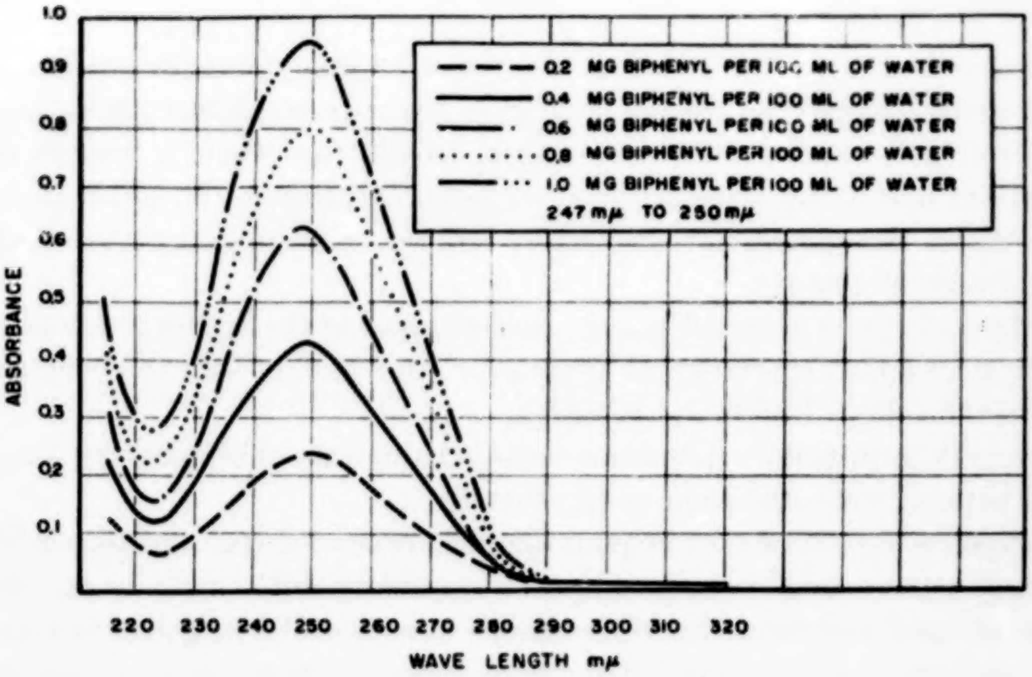

Fig. 2. Biphenyl in water at 55°C.

working limit in milligrams of biphenyl per 100 ml for the ensuing analytical work. Obviously, an error would be made if the test sample contained more than 1 mg of biphenyl/100 ml of water solvent (supersaturation stage).

(The biphenyl solute could be concentrated into a small cyclohexane extract from the aqueous solution but since 0.02 mg of biphenyl may be conveniently determined in aqueous medium, there is no advantage in another extraction step.)

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Effect of temperature upon solution of the sample

Expecting the biphenyl to dissolve more easily in water at higher temperatures, a study was made to ascertain the effect of increased temperature. The respective biphenyl-water tests were placed in a 55°C oven for 20 hours, or in a 90°C oven for 4 hours, or shaken at room temperature for 24 hours.

The absorbance curves for 55° and 90°C are essentially identical (within experimental weighing errors), but the room temperature curves are lower in intensity (Fig. 1). It is desirable then to use the higher temperature methods, since they have nearly the same slope as that of the cyclohexane solvent.

The rate of solution of biphenyl in water at these temperatures was determined. Solution is complete in 40 hours at 55°C in an air oven, in 24 hours at 55° in a water bath, and (in sealed tubes) in 4 hours at 90°C in an air oven.

A variation of the cold water method, completely dissolving the test sample in methyl alcohol and then diluting to volume with water (polyphenyls precipitate) was not satisfactory.

Effect of other polyphenyls

The solubilities of the three isomeric terphenyls in water are much less than that of biphenyl, but mixtures of biphenyl and each of the terphenyls were run to note whether the absorbance of the water solutions might be influenced by the presence of the terphenyls. *m*-Terphenyl and the higher *m*-polyphenyls have their points of maximum absorbance in the neighborhood of 250 mμ.

TABLE I

INTERFERENCES BY POLYPHENYLS, AS SHOWN BY ABSORBANCE MEASUREMENTS

Method	*mg/100 ml*	*Absorbance reading*			
		m-Terphenyl	*p-Terphenyl*	*o-Terphenyl*	*p-Quaterphenyl*
55°C	1	0.030		0.030	
	40	0.061	0.041	0.040	0.022
	50	0.065	0.045	0.030	
90°C	25	0.076	0.055	0.091	

Table I shows that when *o*-, *m*-, or *p*-terphenyl or *p*-quaterphenyl are individually treated with water at 55°C in the absence of biphenyl, that the absorbance is not greater than 0.065. The interference is slightly greater at 90°C. For this reason, 55°C heating is preferred. Biphenyl may, therefore, be determined in mechanical, synthetic mixtures of polyphenyls.

Synthetic mixtures

Three synthetic mixtures of biphenyl, *p*-terphenyl and *p*-quaterphenyl were supplied from an outside source. The sample compositions and recoveries are shown in Table II. Miscellaneous mixtures of pyrolyzed samples are shown in Tables III and IV, in which the determinations of biphenyl by the water solubility method are compared with those by a vacuum distillation procedure and in certain cases by a spot test procedure[5].

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TABLE II

DETERMINATION OF BIPHENYL IN SIMPLE MIXTURE WITH *p*-TERPHENYL AND *p*-QUATERPHENYL

Taken %			*Found %*
biphenyl	*terphenyl*	*quaterphenyl*	*biphenyl 55°C*
5	90	5	5.0, 5.1
10	80	10	9.7, 10.1
20	70	10	20.2, 21.0

TABLE III

DETERMINATION OF BIPHENYL IN PYROLYZED *m*-TERPHENYL SAMPLES

	Biphenyl, %	
Sample No.	*55°C method*	*distillation*
1	0.40, 0.44	0.2
2	0.30, 0.42	0.3
3	0.42, 0.56	0.2
4	0.42, 0.63	0.5
5	0.40, 0.46	0.9
6	0.35, 0.48	0.8
7	0.29, 0.37	0.1
8	0.38, 0.39	0.6
9	0.29, 0.37	0.2
10	0.16, 0.20	0.4
11	0.0	0
12	0.0	0
13	0.0	0
14	0.0	0
15	0.0	0
16	20.4, 21.0	

TABLE IV

DETERMINATION OF BIPHENYL IN PYROLYZED *p*-TERPHENYL SAMPLES

% *Biphenyl*

Sample No.	*55°C method*	*distillation*
A	0.0	0
B	0.0	0
C	0.26	0.1*
D	0.10, 0.20	0.20
E	0.20, 0.20	0.2
F	0.30, 0.30	0.30

* 0.1 by chromatographic method[5].

Sensitivity limits

As little as 20 μg of biphenyl may be determined in a polyphenyl sample of 20 mg. The sensitivity is increased if larger test samples are available.

Field of usefulness for the method

Monsanto Chemical Company is marketing technical grades of *o*-, *m*-, and *p*-terphenyls containing unspecified amounts of biphenyl. The procedure described herein may

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be used to determine the biphenyl content (Table V). Distillation separations are not clearcut, nor as sensitive as the water-solubility method.

TABLE V

DETERMINATION OF BIPHENYL IN TECHNICAL TERPHENYLS

Sample	*Expected*	*Biphenyl %* *55°C*	*Standard deviation*[6]
Santowax-O	0.2	0.18	0.02
(*o*-terphenyl)		0.19	
Lot A		0.20	
		0.20	
		0.22	
		0.22	
		0.24	
Lot B	0.2	0.18	0.02
		0.18	
		0.20	
		0.20	
		0.22	
Santowax-M			
(*m*-terphenyl)	0	0	
Lot C		0	
		0.02	
Lot D	0	0	
		0	
Santowax-P			
(*p*-terphenyl)	0	0	
Lot E		0	
		0	
		0	
Lot F	0	0	
		0	

It was shown in another report[1] that *p*-terphenyl and *m*-terphenyl, when heated, produce varying amounts of biphenyl. The trend of pyrolysis may be followed by this proposed procedure (Tables III and IV). The biphenyl content of mechanical mixtures of biphenyl, *p*-terphenyl, and *p*-quaterphenyl may also be determined by this procedure (Table II).

Calculations of standard deviations[6] and quality of results are included in Table V. In most of the examples, the reproducibility of the results are well beyond the economic or chemical requirements of the project.

SUMMARY

Prior work had shown that the principal products of the pyrolysis of *p*-terphenyl are biphenyl and certain higher polyphenyls. Since the three terphenyls as well as particular higher polyphenyls are being investigated as heat transfer media for atomic energy reactors, the determination of biphenyl, as a major or minor product of their pyrolysis, becomes of prime importance in order to follow the trend of reaction products.

Because of the greater solubility of biphenyl in water, as compared to other polyphenyls, biphenyl is completely extracted from such mixtures by water and can be determined spectrophotometrically in aqueous solution. Effects of temperature, rates of solution, and the presence of polyphenyls were studied. The solubility of biphenyl is about 0.9 mg/100 ml of water, but the suggested working limit in 0.4 mg biphenyl/100 ml of solvent.

As little as 0.1% biphenyl in *p*-terphenyl may be detected and as high as 20% may be determined in higher polyphenyls.

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CHELATE FORMATION OF AMMONIUM AURINTRICARBOXYLATE WITH BIVALENT COPPER

II. MICRO-DETERMINATION OF COPPER BY THE COLORIMETRIC METHOD

by

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In an earlier communication[1], we reported that ammonium aurintricarboxylate (Aluminon) produces coloured chelates with various inorganic cations. We have carried out a detailed investigation of the composition, structure and stability of these chelates[2], and in Part I[3], we have reported our results on physico-chemical studies of the Cupric–ammonium aurintricarboxylate chelate. Aluminon has found wide applications in the colorimetric determination of aluminium and recently Bobtelsky and Ben-Bassat[4] have employed this reagent for the determination of iron, chromium and aluminium by the heterometric method developed by Bobtelsky *et al.*[5,6].

In this paper we have described our results on the application of Aluminon to the colorimetric determination of cupric ions on a micro-scale.

EXPERIMENTAL

Standard solutions of cupric sulphate (BDH AnalaR), and of Aluminon (BDH Reagent), were prepared in doubly distilled water. It was ascertained from the manufacturers[7], that the reagent has been prepared by the method recommended by Smith, Sager and Siewers[8]. The addition of alkali was avoided in the preparation of stock solutions of Aluminon as recommended by these authors. For the spectrophotometric measurements a Unicam SP 500 Spectrophotometer was used with 1 cm glass absorption cells, supplied by the manufacturers. Use was also made of a Klett-Summerson photoelectric colorimeter, where thought necessary, with suitable colour filters. The measurements were conducted in an air-conditioned room maintained at constant temperature of 25°C. The individual solutions were kept immersed in a thermostat at 25° ± 0.01°C. The mixtures were allowed to stand for at least 15 min after mixing to attain equilibrium. Total volume was kept 50 ml in every case.

Validity of Beer's law

It was found that the system obeyed Beer's law in the range of concentration from 1.7 to 100 p.p.m. of copper, when the reagent added was at least 20 times that of the

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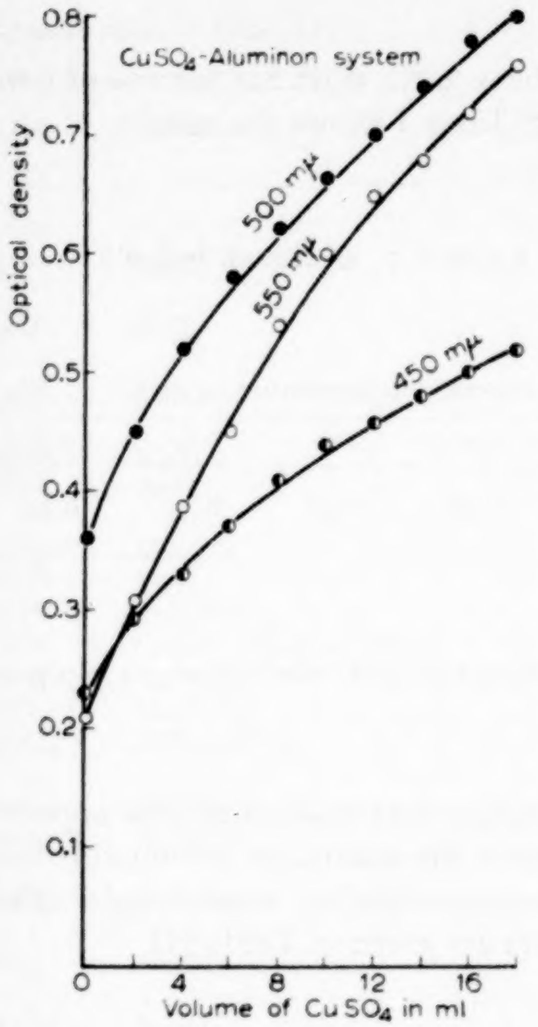

Fig. 1. $CuSO_4$–Aluminon system.

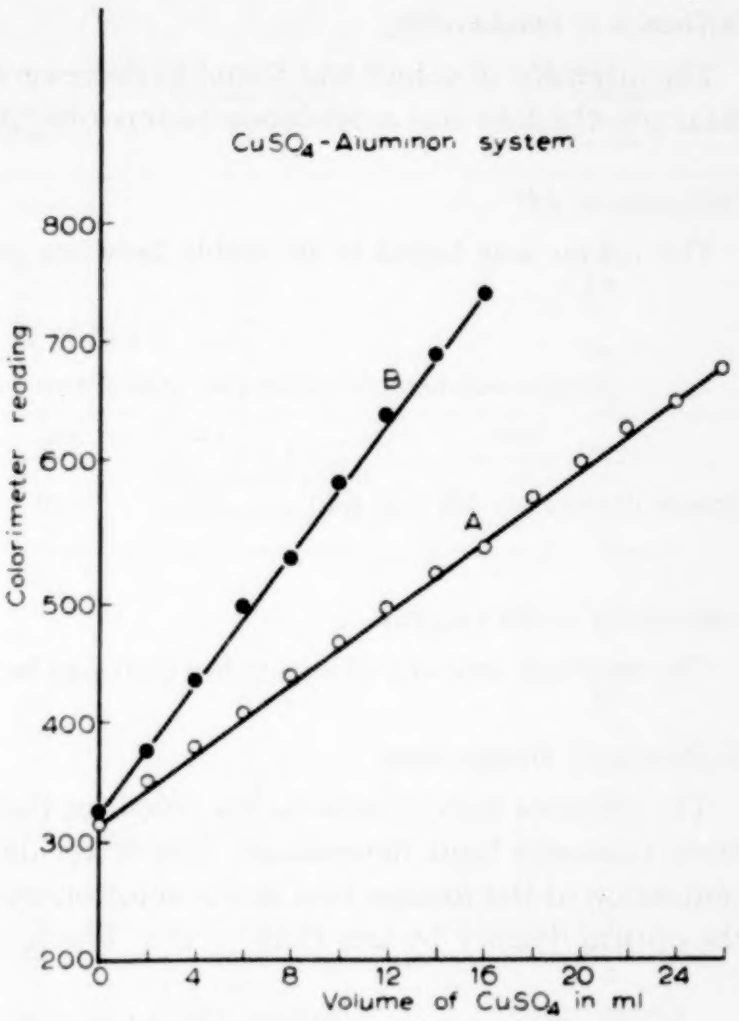

Fig. 2. $CuSO_4$–Aluminon system.

concentration of the metallic ion. The spectrophotometric measurements were carried out at 450, 500 and 550 mμ. The measurement of optical density is not very convenient with a spectrophotometer, when the concentration of the reagent is high and a photoelectric colorimeter was found to be more useful.

Fig. 1 shows the plot of the results obtained with the spectrophotometer. The initial concentration of reagent added in the figures is 10 times the initial concentration of cupric ion. Fig. 2 shows the results obtained with a Klett-Summerson photoelectric colorimeter, using Filter No. 54 green (520–580 mμ). In curve A the concentration of reagent added is 20 times, while in B it is 40 times.

Stability of the colour at room temperature

The colour is found to be stable at room temperature even on prolonged standing. A solution of 0.00005M cupric ion and 0.00025M Aluminon at a pH of 6.00, gave exactly the same optical density at 540 mμ, after 72 h standing time, at room temperature.

TABLE I

(Copper sulphate = 0.00005M; Aluminon = 0.00025M; pH = 6.00)

Temperature °C	*20*	*25*	*30*	*35*	*40*	*45*	*50*
Optical density per cm (540 mμ)	0.580	0.580	0.580	0.575	0.570	0.565	0.550

Influence of temperature

The intensity of colour was found to decrease above 30°C. With further rise of temperature, the lake has a tendency to separate out. Table I shows the results.

Influence of pH

The colour was found to be stable between pH 5.3 to 6.7, as shown below:

TABLE II

(Copper sulphate = 0.00005*M*; Aluminon = 0.0002*M*; temperature = 25°C)

pH	*2.80*	*4.00*	*5.30*	*6.70*	*7.50*	*8.10*
Optical density per cm (540 mμ)	0.23	0.30	0.58	0.58	0.49	0.44

Sensitivity of the reagent

The smallest amount of cupric ion that can be detected with Aluminon is 1.7 p.p.m.

Influence of foreign ions

The effect of various ions on the colour of the chelate was studied and the approximate tolerance limit determined. The latter denotes the maximum permissible concentration of the foreign ions in the solution under investigation, which would affect the optical density by less than ± 2%. The results are given in Table III.

TABLE III

(Copper sulphate = 0.00005*M* (3.1 p.p.m.); Aluminon = 0.00025*M*; pH = 6.00 ± 0.50; temperature = 25°C)

Ion	*Added as*	*Conc. of ion (p.p.m.)*	*Observed change in optical density (%)*	*Tolerance limit (p.p.m.)*
Ag^+	$AgNO_3$	43	+8	0
Tl^+	Tl_2SO_4	163	+6	40
		40	+1.5	
Pb^{+2}	$Pb(NO_3)_2$	83	+7	
		8	+1	
Hg_2^{+2}	$Hg_2(NO_3)_2$	100	−5	
		30	−1.5	30
Hg^{+2}	$HgCl_2$	80	−3	
		30	−1.5	30
Bi^{+3}	Bi oxalate	80	Turbidity	0
Cd^{+2}	$CdCl_2$	45	+5.5	
		15	+2	15
AsO_3^{-3}	H_3AsO_3	125	+7	
		30	+2	30
Sb^{+3}	$Sb_2(SO_4)_3$	57	Turbidity	0
Fe^{+3}	$FeCl_3$	—	Interferes at all concentrations	0
Fe^{+2}	Fe ammon. sulph.	—	,,	0
Al^{+3}	$Al(NO_3)_3$	—	,,	0
Cr^{+3}	$CrCl_3$	20	+8	0
Mn^{+2}	$MnSO_4$	110	No change	Large excess
Zn^{+2}	$ZnSO_4$	130	,,	,, ,,
Ni^{+2}	$NiSO_4$	115	,,	,, ,,
Co^{+2}	$CoSO_4$	115	,,	,, ,,

Continuation of Table III

Ion	*Added as*	*Conc. of ion (p.p.m.)*	*Observed change in optical density (%)*	*Tolerance limit (p.p.m.)*
Ba^{+2}	$BaCl_2$	55	+5	
		10	+2	10
Sr^{+2}	$SrCl_2$	35	+3	
		10	+2	10
Ca^{+2}	$CaCl_2$	16	+3	
		8	+2	8
Mg^{+2}	$MgSO_4$	25	+1.5	25
Be^{+2}	$BeSO_4$	—	Interferes at all concentrations	0
UO_2^{+2}	UO_2SO_4	—	,,	0
Th^{+4}	$ThCl_4$	—	,,	0
Zr^{+4}	$ZrO(NO_3)_2$	—	,,	0
Ce^{+3}	Cerous ammon. sulph.	—	,,	0
Ce^{+4}	$Ce(SO_4)_2$	—	,,	0
WO_4^{-2}	Na_2WO_4	30	+1.5	30
MoO_4^{-2}	$(NH_4)_2MoO_4$	30	—4	
		7	—1.5	7
VO_3^-	NH_4VO_3	2	—8	0
SeO_4^{-2}	K_2SeO_4	570	—5	
		200	—2	200
TeO_3^{-2}	K_2TeO_3	70	—5	
		25	—2	25
CO_3^{-2}	Na_2CO_3	38	—6	
		6	—2	6
SO_4^{-2}	K_2SO_4	140	No change	Large excess
Cl^-	KCl	320	,,	,, ,,
Br^-	KBr	400	,,	,, ,,
I^-	KI	330	—3	
		110	—1.5	110
ClO_3^-	$KClO_3$	510	+3	
		200	+2	200
BrO_3^-	$KBrO_3$	700	+4	
		300	+2	Large excess
IO_3^-	KIO_3	760	+4	,, ,,
		380	+2	
F^-	KF	30	—3	
		10	—2	10
SiO_3^{-2}	Na_2SiO_3	76	No change	Large excess
Citrate	Na_3citrate	59	—6	
		10	—2	10
Tartrate	K_2tartrate	35	—4	
		10	—2	10
NO_3^-	KNO_3	200	No change	Large excess
CNS^-	KCNS	50	,,	,, ,,
PO_4^{-3}	Na_2HPO_4	77	—3	
		30	—2	30
$S_2O_8^{-2}$	$K_2S_2O_8$	24	+5	
		4	+2	4
HCO_3^-	$KHCO_3$	45	—3	
		15	—2	15
$S_2O_3^{-2}$	$Na_2S_2O_3$	24	—8	9
Acetate	NaAc	52	+5	
		8	+1.5	8
$B_4O_7^{-2}$	$Na_2B_4O_7$	49	+4	
		10	+1.5	10

RECOMMENDED PROCEDURE

From a consideration of the experimental results presented here, the following procedure for the colorimetric determination of copper using Aluminon as a reagent is recommended.

A solution of the sample is prepared and treated in the usual way[9,10] to remove other metals present. The pure copper salt solution, as chloride, nitrate or sulphate, thus obtained, is treated directly or in an aliquot portion with at least a twentyfold molar excess of a freshly prepared solution of reagent grade Aluminon in water. The pH of the solution should be adjusted to 6.0 ± 0.5, avoiding free alkali[8], and the solution is diluted to the requisite volume. The mixtures are allowed to stand for 15 min to attain equilibrium. The optical density is then read by using a spectrophotometer with a suitable glass cell at 540 mμ, and compared with the calibration curve. A photoelectric colorimeter with appropriate filter can also be employed. The temperature should be within 20°–30°C.

SUMMARY

The formation of a coloured copper II chelate by ammonium aurintricarboxylate with λ_{max} at 540 mμ may be utilised in the colorimetric determination of cupric ions on a micro-scale. It has been found that, for satisfactory results, at least a twentyfold molar excess of the reagent should be added. The colour intensity can be measured by using a spectrophotometer or a photoelectric colorimeter with a suitable filter.

The colour is stable at room temperature for sufficiently long periods, but the intensity decreases above 30°C. For the formation of a colour suitable for measurement, the pH should be within 5.3–6.7. The smallest amount of copper that can be detected by the reagent is 1.7 p.p.m. Details have been worked out for the use of this reagent, and the interference by various foreign ions has been noted and tolerance limits determined spectrophotometrically.

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A CRITICAL EVALUATION OF COLORIMETRIC METHODS FOR THE DETERMINATION OF PLATINUM METALS. II

by

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In the previous review[1] of colorimetric methods for platinum metals the authors dealt with those papers published prior to 1953. Subsequent to this period there has been a marked upsurge in the volume of literature concerned with this field of analysis. Because some of the new procedures constituted a distinct advance, it seemed of value to integrate these contributions with the previous evaluations. In conformity with former practice the methods are, in general, recorded in order of decreasing sensitivity.

It may be helpful here, to make reference to a deficiency which, to some degree, characterizes all existing colorimetric methods for the platinum metals: indeed, it is true also of colorimetric methods in general. These methods are frequently empirical in principle, involving as they do a more or less qualitative and quantitative duplication of dissolved constituents and of equilibria. It is because of this necessity that the problem of ascertaining the degree of interference from foreign constituents becomes so difficult. In the case of the platinum metals this difficulty is accentuated by the strong tendency of these metals to form a variety of complexes, concerning whose identity there may exist few or no data. Unfortunately, the analytical researcher all too frequently has failed to allow, in the practical development of his procedure, for this tendency toward complexity even though he is aware of its existence.

A further problem, peculiar to the metals of column VIII is the ease of hydrolysis to form insoluble hydrated oxides. Those colorimetric methods which involve heating at pH 4 to 8 are particularly susceptible to this source of error. These two tendencies, together with the more rarely encountered sensitivity to the presence of electrolytes, account for much of the trouble encountered by analysts who seek to apply or even duplicate the various colorimetric procedures for platinum metals.

Adequate recognition of these variables involves some familiarity with the processes for dissolution of the platinum metals. Of these metals, only palladium and rhodium may be quantitatively attacked by single mineral acids. With rhodium, dissolution may sometimes be accomplished with concentrated sulphuric acid, an acid which introduces an interference with the determination of platinum metals, whose character and intensity is seldom, if ever, fully realized. The more general method of dissolving platinum and palladium, ineffective for the other members, is treatment with aqua regia. Here the presence of nitric acid will interfere with most of the classical as well as with instrumental methods of analysis. The use of hydrochloric acid to remove the oxides of nitrogen encourages the formation of various chloro-complexes. The difficulties associated with all of these methods of dissolution are often very much intensified by the presence of the associated base metals.

In so far as dry fusions are concerned, there is the additional and almost unpredictable source of trouble arising out of the amphoteric character of the oxides of the platinum metals, *e.g.* in the sodium peroxide fusion of iridium in a silver crucible.

Consideration of all these factors should convince analytical researchers, particularly in the field of platinum metals, that general statements regarding the degree and kind of interferences should arise only from investigations far more intensive than merely measuring in simple solutions the proportions of contaminant producing a percentage departure from the known value. Thus data dealing with interference from foreign cations based only on the use of solutions of pure salts may be useless or misleading.

PLATINUM

In the initial review[1] the authors dealt with three colorimetric reagents for the determination of platinum: tin(II) chloride, potassium iodide, and thiosemicarbazide. The present discussion includes additional findings concerning these procedures and deals with the following methods: diacetoimidoplatinum, tin(II) chloride, phenylthiosemicarbazide, *p*-nitrosodimethylaniline, hexachloroplatinate ion, thiosemicarbazide, alkali fluoroplatinates.

For general applicability to the determination of platinum the authors prefer tin(II) chloride, and *p*-nitrosodimethylaniline. In spite of claims for other reagents of usefulness with lower ranges of concentration, these two reagents retain superiority from the viewpoints of sensitivity, freedom from interference, range of application and accessibility of descriptive chemistry. Of the two reagents, *p*-nitrosodimethylaniline is the more sensitive, but tin(II) chloride can be applied over a wider range of concentration and there is a lesser degree of interference.

With respect to diacetoimidoplatinum[2] and phenylthiosemicarbazide methods[3] very few data were available to the authors. The former procedure is recorded as applicable to very small amounts of platinum but suffers from, among other things, serious interferences from a large variety of metal cations. Since the range of concentration, 0.02 to 0.09 p.p.m assigned to the reagent indicates a sensitivity greater than any known reagent, additional data concerning the procedure are desirable.

In the case of phenylthiosemicarbazide, the meagre information available indicates a sensitive reagent with the applicable range of concentration as 0.07 to 19 p.p.m. This is surprising in view of the low sensitivity for semicarbazide. Some confirmation of the claim is needed. In any case it is unlikely that the above two reagents will replace either tin(II) chloride or *p*-nitrosodimethylaniline for the colorimetric determination of platinum.

Some additional work has been recorded on the use of tin(II) chloride. MEYER AND AYRES[4] studied the chemistry of the reaction with platinum and found evidence for a variety of reaction products. Precipitation tests with phenylarsonic acid, which may selectively precipitate quadripositive ions, indicated the existence of $[PtSn_4Cl_4]^{+4}$.

They concluded that "chemical evidence at hand is insufficient to warrant an attempt to explain the manner in which the platinum, tin and chloride are bound in the complex". In any case it would appear that the coloured constituents are not colloidal in nature.

MILNER AND SHIPMAN[5] stated, without proof, that at acidities of 1.5 to 2.5N, "a true stannous-platinum chloride complex is formed". At the low acidity originally recommended by SANDELL[6], the reaction was affected by the presence of stannic tin, to the degree that reagent grade stannous chloride produced colours which were not reproducible and were of lesser intensity than colours from technical grade reagent. These authors found also that at the higher acidity the interference from rhodium was less serious and decreased with time. One may conclude from the existing literature that the platinum-stannous chloride colour reaction proceeds most satisfactorily at acidities of the order of 2N and that the identies of the coloured dissolved constituents are unknown. The optimum wave length remains at 403 mμ.

p-Nitrosodimethylaniline is a new reagent for the colorimetric determination of platinum. Previously recommended by YOE *et al.*[7] for the determination of palladium, its use is now extended to platinum[8]. It is a very satisfactory reagent with an optimum concentration range of 0.7 to 2.4 p.p.m. The absorbance of the coloured dissolved constituents is measured at 525 mμ and remains constant for at least 24 hours. In order to obtain uniform development of the orange-red colour it is necessary to use a large molar excess of reagent over platinum and to standardize the volume of solution, the time of heating, the acidity, and the concentration of buffer reagent. The extent of interference from cations and anions is about that of the tin(II) chloride or iodide methods. There is evidence for the existence of at least two coloured species as reaction products, one of which, when isolated, had the composition

$$\mathrm{Pt}\,[(\mathrm{CH_3})_2\mathrm{N{-}C_6H_4NO}]_4\mathrm{Cl_2}$$

In a second paper YOE AND KIRKLAND[9] record procedures for the colorimetric determination of platinum and palladium without a separation of the two metals. The method involves the determination of palladium in one sample aliquot by its colour reaction with p-nitrosodimethylaniline at room temperature[10] while a second aliquot heated as described above gives a total colour from both platinum and palladium. Absorbance was measured at 525 mμ, Beer's law was obeyed, and maximum accuracy was found over the range 0.25 to 1.00 p.p.m. of palladium. Absorbance is sensitive to changes of acidity but remains constant with sodium acetate-hydrochloric acid buffers over the narrow range of pH 2.2 ± 0.2. The method can be applied to advantage in the analysis of many ores and concentrates where the proportions of platinum and palladium are of about the same order. To the degree that these proportions differ, the usual increase in error of the amount of the minor constituent is encountered. In order to enlarge the scope of the method to include very large proportions of palladium, the authors introduced a differential modification. This procedure involves the use of a reference solution salted with palladium to an amount slightly less than that present in the sample. The authors also separate palladium from platinum by a chloroform extraction of the palladium p-nitrosodimethylaniline complex. A considerable disadvantage of this method is the necessity of using chemically pure chloroform. The reason for this is not known.

The problem of separating platinum together with palladium from associated platinum metals is met by the solvent extraction with benzene of the diethyldithiocarbamate complexes[11]. At the present time, this method of separation is of very limited use. The effect of associated base metals is not known and it is quite unlikely that, for the isolation of the platinum metals, the procedure can compete with the collective and selective isolation of base metals by hydrolysis from a nitrite solution with or without a carrier. Furthermore, there is restricted separation of palladium in the presence of rhodium and iridium.

More recently data have been obtained relative to the character of the solvent for *p*-nitrosodimethylaniline. KIRKLAND AND YOE[8] point out that the alcohol used as a solvent must be freshly distilled, otherwise the reagent is discoloured during the heating process. It has since been found[12] that aqueous solutions of *p*-nitrosodimethylaniline afforded a precision markedly better than that obtained with alcoholic reagent. In this procedure, samples buffered at pH 2.2 were heated for 2.5 minutes at 85°C and diluted to 50 ml volume. Transmittancy was measured in a 5 cm cell at 515 mμ. The disadvantage of the aqueous medium arises from instability made evident by a recurring deposit from the reagent solution. This eliminates an exact knowledge of reagent concentration and necessitates the creation of standards for each lot of reagent. The relative value of the alcoholic and aqueous reagents would appear to depend largely upon personal preference. The authors preferred the aqueous reagent for solutions free from palladium because of the improved precision. Recent data obtained in the authors' laboratory provide some evidence that an acidified aqueous solution of *p*-nitrosodimethylaniline will retain the improved sensitivity and avoid the instability.

For the concentration range 3–11 p.p.m. KIRKLAND AND YOE[13] recorded a photometric procedure based upon the measurement of the ultra-violet absorption maximum at 262 mμ of the hexachloroplatinate ion. The solutions of this ion buffered at about pH 5 are stable for several hours and absorbance measurements can be made with a precision of ± 1%. Methods of this type suffer from excessive interference and they will find little application to the analysis of naturally occurring platinum. Where compositions of the platinum-bearing material are relatively simple, the method has the advantage of good sensitivity.

Other halogen–platinum metal complexes have been reported to form light-absorbing dissolved constituents which obey Beer's law, *e.g.* dilute solution of fluoroplatinates of alkali metals excepting sodium[14]. Recent work in the authors' laboratory supports the suspicion that, in some cases at least, the equilibria involving these halogen complexes are sensitive to the full range of influences such as salt concentration, acidity, temperature, and a wide variety of impurities. As one might expect, the progression within the halogen family toward the heavier halide results in a corresponding shift in maximum absorbance toward the longer wavelength. While this effect could result in decreased interference of impurities, the sensitivity of the absorbance to other influences is a discouraging feature.

Thiosemicarbazide was used by DE TRECCO[15] for concentration ranges of 10–90 p.p.m. of platinum. The author included few data and, because of the very desirable colour, the method was examined further[16]. A maximum absorbance was found at 585 mμ; and a pH of 6.4 was found to be optimum for the final solution. This acidity is not an encouraging factor since instability due to hydrolysis is induced. Indeed, and perhaps prematurely, the procedure was abandoned when a lack of reproducibility and a high degree of interference from small amounts of associated base metals became evident. BARCOVSKII AND KUL'BERG[17] examined the reaction between platinum and thiosemicarbazide in alkaline solution and reported that the resulting intense coloration was due to a dissolved pure substance. The suitable range of concentration was reported as 100 to 1000 p.p.m. and there was no interference from considerable amounts of gold, iridium and rhodium. It is not improbable that this method may yet prove useful.

PALLADIUM

Among the platinum metals the analytical methods for palladium, both classical and instrumental, are relatively numerous. Nine colorimetric methods were discussed in the previous review. The following seven reagents are included in this review: 3-hydroxy-1-*p*-sulphonato-phenyl-3-phenyltriazine, 2-nitroso-1-naphthol, *α*-furildioxime, thiourea, ethylenediaminetetraacetic acid (EDTA), the catalytic formation of molybdenum blue, rubeanic acid.

For concentration ranges of about 0.2 to 6 p.p.m. of palladium SOGANI AND BHATTACHARYYA[18] claimed superiority over other colorimetric reagents for 3-hydroxy-1-*p*-sulphonato-phenyl-3-phenyltriazine. The method does offer certain advantages. The reagent, and the presumably yellow palladium complex $(C_6H_5\text{-}N_3OC_6H_4SO_3H)_2Pd$ are soluble in aqueous media. The reaction is almost instantaneous and relatively insensitive to acid concentration, having an optimum range of pH from 2.5 to 4.4 for sulphuric or hydrochloric acid solutions, and of 1.7 to 4.4 for nitric acid solutions. To encourage specificity, a range of 2.5 to 3.0 was recommended. The colour was stable for at least 24 hours, and variations of temperature between 25° and 85° C were without effect. Full colour development was ensured at molar ratios of 1 of palladium to 8 of reagent. Although maximum absorbance occurred at 413 mμ, measurements made at 420 or 430 mμ respectively decreased and eliminated interference from reagent absorbance. Beer's law was obeyed in all cases. The authors' claims for superior specificity are inadmissable. Aside from the fact that their method of determining the effect of diverse ions allows limited predictions, the data presented indicate the necessity of a preliminary separation of platinum metals except perhaps in the relatively few instances where determinations involve solutions of simple composition. In so far as one may be concerned with the presence of salt, or of associated base metals, the proposed method offers little or no advantage over several of the established procedures. However, in spite of these not uncommon deficiencies, the new procedure should prove useful.

Useful new data have been supplied by CHENG[19] for the colorimetric determination of of palladium by 2-nitroso-1-naphthol. The sensitivity toward palladium of this reagent was about equal to that of 1-nitroso-2-naphthol, but with the former reagent interferences from such associated metals as copper, chromium, nickel, cobalt and iron were eliminated by complexing with EDTA. There was no interference from other platinum metals. As one might expect, the sequence of addition of reagents was a significant variable. The applicable range of concentration was about 1 to 5 p.p.m. and the optimum wave length was 370 mμ. There was no change in absorbance from pH 1.5 to 3.5; and the colour remained stable for at least 4 hours. Contrary to the previous findings, the development of colour at the temperature of a boiling water bath was unsatisfactory, encouraging as it did the development of a precipitate in the extractant. Toluene was used for the extraction, with the excess of the yellow coloured reagent dissolving in the alkaline aqueous layer. The author prefered inducing alkalinity by ammonium hydroxide rather than sodium hydroxide, since use of the latter encouraged the precipitation of base metals. This colorimetric method possesses many favourable factors and will find increasing applications.

An interesting variation in the 2-nitroso-1-naphthol method is suggested by the work of PESHKOVA, SHLENSKAYA AND RASHEVSKAYA[20]. These authors were interested in the applications of various oximes to the determination of palladium. It was found that the addition of β-napthoquinone and hydroxylamine to a solution of palladium resulted in an inner complex formation of the latter with 2-nitroso-1-naphthol.

The interest in the use of oximes for the determinations of palladium has its origin in the fact that dimethylglyoxime and its analogues are the only reagents for any platinum metal which approach specificity. From time to time various derivatives are examined with a view to application for gravimetric or colorimetric determination. Absorption spectra for palladium complexes with 4-methyl- and 4-*iso*propyl-1,2-cyclohexanedione dioxime were recorded by HOOKER AND BANKS[21].

α-Furildioxime was used by MENIS AND RAINS[22] to produce a yellow-coloured complex which in aqueous–alcohol medium obeys Beer's law at 420 mμ. Presumably the method involves the incipient formation of an insoluble complex and consequently emphasis is placed upon the order of addition of reagents, the temperature of the solution, the necessity of an excess of reagent and the upper limit of palladium content. The procedure requires the addition of ethyl alcohol to increase the maximum working range from 30 to 120 μg of palladium per 25 ml final volume. Excess alcohol is also detrimental. In aqueous media, containing 10% by volume of ethyl alcohol and low concentrations (1 to 5 p.p.m.) of palladium, the colour was stable for at least 20 min but, as would be expected, stability decreased, with increasing amounts of palladium. The optimum acidity was 0.1 to 1.4*N* hydrochloric acid, and the authors stated that "concentrations as low as 0.1 p.p.m. of palladium could be determined in 5-cm cells". The authors record interference only from cyanide and various coloured ions such as ruthenium, rhodium, iridium, platinum, gold, etc. Their statement that these metals "do not form a complex with the reagent" is not acceptable without experimental data, none of which are provided.

To avoid interference an alternative method is provided, and in the authors' opinion it will be more generally acceptable. With this procedure the palladium complex, developed in the absence of ethyl alcohol, is extracted with chloroform. The absorbance of the coloured organic extract, freed from water by the addition of sodium sulphate, is measured at the absorption peak of 380 mμ. Undoubtedly these two procedures are worthy of consideration, but any claim of superiority over the more firmly established methods for comparable ranges of palladium concentration will require further substantiation. In any case, with this platinum metal the greater need is for more efficient methods of isolation, rather than for slight improvement in sensitivity.

For the concentration range of 0.8 to 24 p.p.m. of palladium, NIELSCH[23] used thiourea in 10% hydrochloric acid. The optimum proportions of the acid or of the reagent were not critical in the range of wave lengths of 360 to 380 mμ, and the colour remained constant for several hours. The effect of associated impurities was not reported, but one can assume that interferences would be objectionably extensive. In its present stage of development the method is not recommended.

While CHENG[19] makes no reference to the possible existence of an EDTA complex with palladium, it is interesting to note that EDTA was used by MACNEVIN AND KRIEGE[24] as a colorimetric reagent for palladium. The ratio of EDTA to metal was 1 : 1 and remained unaffected by as much as a ten-fold excess of reagent. Beer's law is obeyed over the range 5 to 200 p.p.m.; the colour is not objectionably sensitive to the ionic strength of the solution; develops quickly, and is acceptably stable. However, the method requires an adjustment of acidity at pH either 7 ± 1 or 1.8 ± 0.2. For the former, the wavelength 337 mμ is used and for the latter 377 mμ. The data concerning interferences by other platinum metals indicate that an isolation of palladium would be required. It is proposed to use the reagent dimethylglyoxime for the separation of palladium, the complex then being treated only with aqua regia and hydrochloric acid. While the authors commendably suggest that the method will find its principal application to relatively pure solutions of palladium, there is little doubt that it may form a very useful part of "schemes of determination".

Further work has been recorded on the adaptations of the catalytic properties of platinum metals to produce coloured constituents, the absorbance of which is used as a measure of the quantity of the metal present in solution. For the determination of palladium, SHIOKAWA, KAMBARA AND YAGI[25] determined the time required for various μg amounts of palladium to produce a given transmittance through solutions of molybdenum blue developed from molybdate and sodium dihydrogen phosphate. The method can be applied over the range 4 to 11 μg of palladium, but a deterrent to the general use of procedures such as this are the serious interferences. It is unlikely that this method will replace any of the very acceptable methods for the determination of palladium.

A method for palladium for which high sensitivity is claimed was recorded by XAVIER AND RAY[26]. The procedure involves an extraction into *iso*-amylalcohol of the yellow product of a reaction between palladium, pyridine and rubeanic acid (dithiooxamide). The aqueous solution was adjusted to a pH below 7 and contained EDTA to eliminate interference from iron, cobalt and nickel.

IRIDIUM

In the previous review[1] the authors were able to recommend only one colorimetric method for the determination of iridium. The following seven new methods have since been recorded, all of which can be useful when applied under appropriate conditions: Leucocrystal violet, stannous bromide, *p*-nitrosodimethylaniline, *o*-dianisidine, ethylene-dinitrilo-tetracetic acid, ceric sulphate, tetraphenylphosphonium bromide. These allow applications to a variety of commonly occurring ranges of concentration. While there is a tendency among authors to over-emphasize the problem of sensitivity, in the case of iridium its significance is clearly evident. Iridium is one of the relatively minor constituents of platinum metal deposits and practically all direct determinations require methods sensitive to its presence and to variations in its proportions.

Two methods are proposed which claim an optimum minimum concentration of 0.5 p.p.m. AYRES AND BOLLETER[27] used solutions of leucocrystal violet in 1 *M* phosphoric acid. The iridium solution was prepared for analysis by the addition of perchloric, nitric and phosphoric acids and fuming to the absence of perchloric acid. Subsequent to cooling, the solution was diluted and boiled again in order to obtain maximum and reproducible absorbance by the yellow oxidation product of leucocrystal violet produced in an acetate-buffered solution. Measurements were made at 590 mμ and the optimum range of concentration was 0.5 to 4 p.p.m. The experiments made to determine the effect of associated impurities were well arranged and the authors reached the conclusion that there was "no interference from other platinum elements unless they are present in large amounts relative to the iridium". The difficulty lies in the fact that, with practically all natural deposits, it is just this condition which exists. Interference from gold was eliminated by a useful combination of established methods, but the presence of iron required prior removal. Excess of sulphate ion also interfered in the development of colour.

A second procedure encompassing the same range of concentration (0.5 to 5 p.p.m.) is recorded by BERMAN AND McBRYDE[28]. This method suffers from excessive interferences, the effects of which can in some instances be removed readily, but in general a rather complete isolation of iridium is a necessity. There is some considerable value in the tolerance for sulphuric acid, a reagent which, in many schemes of analysis, frequently permits no substitution in that it is the only acid solvent for rhodium, the rather constant companion of iridium. In this connection it is well to realize that the degree of interference from sulphate ions must be determined subsequent to the process of fuming. The mere addition of sulphuric acid does not necessarily introduce a comparable degree of interference. From this point of view the proposed method is particularly suitable when complex materials are to be treated. The intense yellow colour with an absorption peak at 402 mμ is obtained by heating solutions of tin(II) chloride and iridium salts in a medium of hydrobromic acid. Tin(II) bromide could be used to increase the sensitivity but there was a decrease in stability. Unfortunately, the method is particularly sensitive to variations in procedure, such as time of contact, temperature, quantity of reagent and of hydrobromic acid. On the other hand there is an advantage in the time required for a determination. The method is rapid and can be applied immediately to a wide variety of analytical schemes which provide for the isolation of iridium. Of particular interest is the application to a solution of iridium resulting from the separation of rhodium by antimony[29].

For the determination of iridium in the range of 1.5 to 10 p.p.m. WESTLAND AND BEAMISH[30] used *p*-nitrosodimethylaniline to produce a cherry red complex of unknown composition. The method offers no specificity among the platinum metals and there is interference from non-volatile acids. To avoid the latter, a new separation was devised which involved the hydrolytic precipitation of iridium in the presence of nickel hydroxide as a carrier. The latter cation was subsequently removed by passing the re-dissolved precipitate through a column of Dowex-50 ion exchange resin. This colorimetric method is sensitive to various factors such as temperature, acidity, time of heating, and ionic strength. In addition, it is necessary to standardize the character of the dissolved constituents immediately prior to the determination. Measurements were made at 530 mμ with an alcohol–water solution of iridium buffered at pH 7.2 to 7.3 previously heated for 40 min in a water bath at 70°C. This procedure can only be recommended with reservations. The preparation of the coloured dissolved constituent can be attended by hydrolysis of iridium and although the authors were able to redissolve the precipitate prior to measurement of absorbance there always remained the possibility of resistance to re-dissolving.

Control of the amount and often of the character of the coloured complex is one of the great difficulties encountered in the colorimetric analysis of platinum metals. Of the latter none is more susceptible to change than an iridium solution, and of the seven methods available none is more sensitive to change of conditions than the *p*-nitrosodimethylaniline reagent. The authors feel that of the above three methods this reagent has the least to commend it.

A colorimetric procedure for ranges of 2 to 20 p.p.m., somewhat more advantageous than the *p*-nitrosodimethylaniline method, was recorded by BERMAN, BEAMISH AND MCBRYDE[31]. Solutions of iridium chloride buffered at pH 4.3 and treated with *o*-dianisidine produced an orange colour which changed to purple upon adding concentrated hydrochloric acid. Measurements of the stable colour were made at 530 mμ. Sulphuric acid solutions could not be used and there was interference from associated metals and from oxidizing reagents. The absorbance was sensitive to the amount of reagent and to the acidity of the medium in which the colour was developed. On the other hand the method is rapid and the technique is simple.

For concentrations of iridium of 5 to 60 p.p.m., MACNEVIN AND KRIEGE[32] added the sodium salt of ethylene-dinitrilo-tetracetic acid to solutions of quadrivalent iridium at a pH of 11.4 to 11.6 and heated at 80 to 90 °C. Absorbance was measured at 313 mμ; the colour of the unknown complex remained stable at room temperature for 12 hours. The fact that a strongly basic medium is required, is not an encouraging feature from the point of view of interferences, particularly for the not unusual case when determinations must be made on iridium solutions containing traces of base metals. The authors record that all of the platinum metals interfere but that addition of sulphate was without significant effect. The latter conclusion may have no significance since the addition of sulphuric acid to solutions of the metals is usually made with a view to subsequent fuming, a process which may introduce an interference not duplicated by the mere addition of sulphate. It should be noted also that the degree of interference from platinum metals is not necessarily ascertained in the absence of a duplication of methods of dissolution. The advantage of the proposed method lies in its speed and ease of application and its rather useful range of optimum concentrations of iridium, although the fact that measurements are made in the ultra violet region imposes a limitation on the method based on the instruments available.

The most selective colorimetric method for iridium remains that recorded by AYRES AND QUICK[33]. Unfortunately, there is considerable difficulty in achieving control of the equilibria involved in the development of the coloured constituent. MAYNES AND MCBRYDE[34] discussed the effects of these difficulties and proposed a somewhat similar method which presumably was capable of improved precision. The procedure involved an oxidation of the iridium sulphate solution by ceric sulphate to produce a red constituent of unknown composition. Measurements were made at 510 mμ.

Two procedures were used: in one, subsequent to cooling, the fumed solution was treated with water and ceric sulphate, and heated for at least 12 hours at 70 °C. The second procedure involved heating at 92 °C for six hours. While the authors were able to obtain satisfactory precision, continued use of the method has revealed a tendency toward variable results, undoubtedly due to the difficulty of duplicating the factors which influence the colour development. In any case, while the range of iridium concentrations, 2.5 to 25 p.p.m. is a useful one, the method cannot be considered as entirely satisfactory. The freedom from interference, particularly from base metals, is a good feature. On the other hand the effects of nitric acid are serious, and since this acid is very often used at some stage in the procedure prior to the determination of iridium, and since fuming with sulphuric will not necessarily remove traces of nitric acid, it may well be that there is here a partial explanation for lack of precision. Compared to the method of AYRES AND QUICK[33] there is also a somewhat greater interference from some of the platinum metals.

The authors[34] also recorded a procedure for the determination of rhodium and iridium present in the same solution. This method will have limited application and one may expect to encounter difficulties with deposits of a rhodium residue which resists dissolution. In any case these procedures[33,34] require a greater understanding of the character and behaviour of the dissolved constituents, and until more information is available one may not anticipate a generally successful method involving the principle of oxidation.

A potentially useful colorimetric method for the determination of iridium has been recorded by NEEB[35]. Large proportions of rhodium to iridium can be tolerated. The author used the procedure for the ranges 2.4 to 60 p.p.m. in a 2 cm cell, and 1.5 to 15 p.p.m. in a 5 cm cell. The yellow complex was formed with quadrivalent iridium and tetraphenylphosphonium bromide, extracted with chloroform, filtered, and the absorbance measured at 500 mμ or with appropriate filters. An absorbance peak also occurred at 450 mμ. As one would expect, the method required careful control of acidity and of salt content. The amount of excess reagent and the volume of the aqueous solution were not critical. There was interference from nitrate, sulphite and perchlorate. With the notable exception of rhodium, all of the platinum metals interfered. No data concerning the effect of associated base metals, nor of the precision of the method were recorded.

Undoubtedly, the procedure should receive further attention.

Of the eight published methods for the colorimetric determination of iridium none can be compared favourably with the tin(II) chloride method for platinum.

RHODIUM

Relatively little new has been recorded concerning the colorimetric determination of rhodium. In experienced hands tin(II) chloride has been recognized as one of the most useful reagents for ascertaining the presence of a number of platinum metals including rhodium. Nevertheless, its application to the quantitative estimation of rhodium has only recently been fully realized. Various authors have proposed its use and have suggested procedures for specific purposes. The most detailed examination of this procedure has been recorded by AYRES, TUFFLY AND FORRESTER[36]. These authors record the optimum range of concentration as 4 to 20 p.p.m. Measurements are made at 475 mμ. The pink or red constituent, of unknown composition, is developed within a few minutes by heating near the boiling point. The colour is very stable, and is unaffected by wide variations in the proportions of hydrochloric acid and tin(II) chloride. As one would expect, there is considerable interference from other platinum metals and their removal is necessary. Towards this end, the authors suggest various standard solvent extraction procedures. Of the associated base metals, large proportions of nickel can be tolerated. A procedure is recommended for the simultaneous determination of rhodium and platinum; measurements being made at 473 and 403 mμ, or in order to reduce the absorbance of platinum in the presence of rhodium, at 560 and 403 mμ. Determinations such as these have limited applications, and are subject to large per cent errors when there is a preponderance of one constituent as is usually the case with rhodium and platinum. The tin(II) chloride method was also examined by MAYNES AND McBRYDE[37], and their procedure was used successfully by CHENELEY, OSMOND AND PERRY[38] for rhodium concentration as low as one p.p.m.

These authors[38] found difficulties with the 2-mercapto-benzoxazole[39] method. A modified procedure permitted precise measurements of the acetone extract at 335 mμ.

In the opinion of the authors the tin(II) chloride method is the most generally satisfactory for the colorimetric determination of rhodium. Most certainly there is a need for additional reagents and particularly reagents with greater sensitivity.

OSMIUM

Until very recently, thiourea was the only colorimetric reagent for osmium recorded in the literature. WINGFIELD AND YOE[40] have recently proposed the application of 1-naphthylamine-3,5,7-trisulfonic acid to produce a stable violet complex with sexivalent osmium. Maximum absorbance occurred at 560 mμ. Excess reagent was unimportant provided a ratio of 7:1 was not exceeded. The coloured constituent contained osmium and reagent in the ratio of 1 to 2. The amount of the coloured complex was sensitive to reaction time and to acidity; constant absorption was attained subsequent to 4 h and maximum absorbance occurred at pH 1.5. Beer's law was obeyed up to 6 p.p.m with a suitable working range of 1.5 to 5.5 p.p.m. The method was not selective, requiring a preliminary separation of osmium(VIII) oxide by distillation with nitric acid. Early difficulties involved the quantitative preparation of sexivalent osmium and the authors dealt with this by the adjustment of hydroxyl ion in the presence of the reagent. The data dealing with this aspect of the problem have not yet been published. Perhaps the principal criticism of the method is concerned with the use of nitric acid which interferes with subsequent distillations of small amounts of ruthenium, a metal which is practically always present with osmium as a minor constituent in natural occurrences of platinum metals. The usual methods for the removal of nitric acid prior to the distillation of ruthenium can result in small losses of the latter and since it is with the application to small amounts of constituents that colorimetric methods find their chief justification, the nitric acid distillation of osmium can be a source of considerable difficulty.

Further researches involving the use of thiourea for osmium have been recorded by SAUERBRUNN AND SANDELL[41,42]. These authors[41] show that the red dissolved constituent formed when osmium(VIII) oxide reacts with thiourea in an acidic medium is best represented as trivalent ion $[Os(NH_2CSNH_2)_6]^{+3}$. This is contrary to some of the earlier published data which recorded a similar complex with osmium in the quadrivalent state. In a second publication[42] the authors record the details of an interesting method for determining osmium with thiourea in the presence of ruthenium. The latter is maintained in the reduced state by the addition of iron(II) sulphate while osmium is oxidized by nitric acid, and subsequently extracted with chloroform. The latter extracts are combined and treated with a sulphuric acid solution of thiourea and the colour measured at 480 mμ. The method is suitable for amounts of 5 to 1000 μg of osmium. Chloride ion interferes through the formation of chloro-osmate which resists oxidation to the octavalent oxide. When the presence of chloride is unavoidable, it can be removed by gentle fuming with sulphuric acid in the presence of ferrous sulphate. Acceptable results were obtained in the presence of large proportions of Fe^{+2}, Cu^{+2}, Pd^{+2}, and Pt^{+4}.

The same authors[43] applied the technique of this extraction procedure to the determination of as little as 0.005 μg of osmium at a dilution of 1 to 10^9. The method is catalytic in principle and involves the prior determination of the effect of varying quantities of osmium(VIII) oxide on the rate of reaction between ceric ammonium sulphate and an arsenic(III) salt. Subsequent to the quick addition of an aliquot of ceric salt to the solution of arsenic(III) and osmium tetroxide, previously extracted from the chloroform solutions, the time required to reach a transmittance of 40.0%, measured at 340 mμ, was determined. The method was quite sensitive to temperature changes, and variations of temperature beyond ± 1°C produced errors exceeding 5%. The authors report recoveries of better than 90% for 0.01 to 0.2 μg of osmium in 25–50 ml solution. As would be expected the determination is subject to considerable interference from a wide variety of dissolved constituents and will find application only where the osmium has been separated. Of course the accompanying solvent extraction procedure will ensure a reasonably good degree of isolation.

A second very promising extraction procedure was recorded by NEEB[44]. Here there is the advantage that the osmium is in the form of the hexachloro salt. A yellow complex is formed with tetraphenyl phosphonium chloride in a medium 0.2 to 0.3N in hydrochloric acid and subsequently extracted by, and the absorption measured in, a chloroform medium. Since the partition coefficient is not favourable, complete recovery is only accomplished by a number of separations. An alternative procedure, involving a single extraction, can be used provided the conditions are carefully duplicated and standards similarly prepared. The range of osmium concentrations used was about 0.3 to 1.5 p.p.m. with a 2-cm light path. Maximum absorption occurred at 346 and 375 mμ. Measurements made with the latter wavelength avoided some of the interferences which were relatively significant at 346 mμ. Sulphite, perchlorate, and constituents which were precipitated by the reagent and subsequently extracted, interfered with the determination. These difficulties are not particularly significant since osmium is readily isolated from practically all associated elements except ruthenium. Since the latter metal may be tolerated in proportions of 100 to 1, the method may be of considerable importance. Furthermore, there is the advantage that sulphate ion does not interfere. Rhodium is also without effect. Undoubtedly this procedure should be examined further to determine its precision and its applicability to the various types of solutions encountered in the normal course of separations of platinum metals.

RUTHENIUM

Reagents for the colorimetric determination of ruthenium are relatively numerous. Only one new procedure has been recorded and its application is confined to amounts which may be determined by the classical methods which, of course, provide greater accuracy. However, when high accuracy and precision is of secondary importance and large numbers of determinations are to be made, the procedure will be quite useful. In this method, STONER[45] used the greenish-yellow colour of potassium perruthenate for ranges of 0.1 to 12 mg in a final volume of 100 ml. The octavalent oxide was distilled from a mixture of perchloric acid, phosphoric acid, sodium bismuthate and a trace of chloride into a solution of potassium hydroxide. Subsequent to dilution and a half-hour standing, measurements were made at 380 mμ. It is assumed that the distillation results in the evolution of chlorine which in the caustic distillate forms hypochlorite and thus, by oxidation, perruthenate is produced. Since hypochlorite absorbs strongly at 296 mμ, the amount of this anion developed in the caustic medium must be kept at a minimum through careful control of the chloride ion in the distillation flask. In addition to the chloride ion, small amounts of nitric acid interfere. The author assumes that all of the hydrochloric or nitric acids, used for the preparation of the sample, may be removed by fuming with sulphuric acid. This is seldom the case; intermediate treatments with water are almost always required to remove the nitric acid.

The procedure was applied successfully to uranium alloys containing neodymium, zirconium and molybdenum, the presence of the latter requiring the addition of phosphoric acid to the distilling mixture. In spite of the claim to a superior colour stability, this perruthenate method offers little or no advantage over the older ruthenate procedure, the latter being applied over the range 6.5 to 64 p.p.m. Furthermore, the author's statement that osmium is the only interfering element is surely incorrect.

SUMMARY

This paper is the second review of quantitative colorimetric methods for the six platinum metals and covers the period from May, 1953 to March, 1957. Each method is evaluated from the point of view of the optimum concentration range, specificity, and practical applications to the assay for platinum metals.

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SPECTROPHOTOMETRIC DETERMINATION OF COBALT WITH ISONITROSODIMEDON

by

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INTRODUCTION

Guha-Sircar and Bhattacharyya[1] introduced isonitroso-dimethyl-dihydroresorcinol (isonitrosodimedon) as a gravimetric reagent for cobalt. Shome[2] showed that this reagent was also valuable for the colorimetric determination of cobalt, whereas Gillis, Hoste and Pyck[3] investigated the micro-gravimetric determination with good results.

As it was found that iso-amylalcohol extracts the isonitrosodimedon cobalt complex, this procedure was investigated to achieve a more specific and sensitive determination.

TRANSMITTANCY CURVE OF THE ISONITROSODIMEDON COBALT COMPLEX IN ISO-AMYLALCOHOL

To determine the wavelength of maximal absorption and the molar extinction coefficient of the complex, the transmittancy was measured as a function of the wavelength.

Procedure

Place in a separatory funnel 25 ml of a cobalt solution containing 2 μg Co/ml, the pH being adjusted at about 6 with an adequate buffer (see below). The solution is extracted successively with one 10 ml and two 5 ml portions of isoamylalcohol containing 0.025 % isonitrosodimedon, shaking each time for 3 min. The iso-amylalcohol fractions are collected in a 25 ml graduated flask and made up to the mark with ethanol. The use of the latter avoids the formation of a cloudy solution due to water droplets and does not affect the transmittancy curve. The transmittancy curve is registered *versus* a blank with a DR-Beckman recording spectrophotometer using 1 cm matched quartz cells and a tungsten lamp.

The results are represented in Fig. 1, curve 1, whereas curve 2 represents the transmittancy curve of the reagent at a concentration of 0.02% *versus* iso-amylalcohol as a blank. The wavelength of maximum absorption of the complex is at 374 mμ where the absorption of the reagent itself is quite small. At 374 mμ the molar extinction coefficient has a value of:

$$a_M = \frac{0.664 \times 58.94}{2\cdot 10^{-3}} = 19{,}680$$

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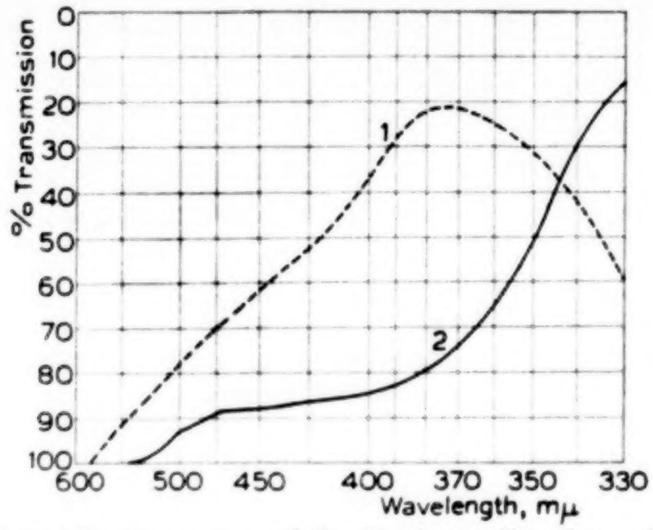

Fig. 1. (1) Transmittancy curve of the isonitrosodimedon cobalt complex.
(2) Transmittancy curve of the reagent.

The wavelength of maximum absorbancy is in disagreement with the value proposed by SHOME (480 mμ).

From our measurements it appears that isonitrosodimedon is a more sensitive reagent than the nitroso-R-salt in current usage. OVENSTON AND PARKER[4], for instance, state that 2 μg Co/ml has an absorbancy of 0.500 at 500 mμ, corresponding to a molar extinction coefficient of 14,710. Isonitrosodimedon has moreover the advantage of giving instantaneous complex formation, whereas nitroso-R-salt needs accurately controlled heating to achieve complete complex formation.

DISTRIBUTION COEFFICIENT

To be able to determine the number of extractions required to achieve quantitative extraction of the complex for a given water–isoamylalcohol ratio, the distribution coefficient was determined, using radioactive ^{60}Co as a tracer.

Procedure

Place in a separatory funnel 10 ml of a buffer solution (pH = 6), 1 ml tracer ^{60}Co of high specific activity, add 10 ml isoamylalcohol containing 0.025% reagent and shake for 3 min. After separation, 4 ml of each phase are counted, using standard vials and a well-type NaI (Tl) scintillation counter. The results of two experiments are summarized in Table I.

TABLE I

Solution	*Counts/min/ml*	*Distribution coeff.*
Buffer	262	
Isoamylalcohol	18,069	68.9
Buffer	259	
Isoamylalcohol	17,767	68.7

The experiments show that three extractions using successively one 10 ml and two 5 ml portions isoamylalcohol are largely sufficient to achieve quantitative extraction from a 25 ml aqueous phase.

STABILITY OF THE COMPLEX

To investigate the stability of the color, the absorbancy was measured during a 17-h period. The results are summarized in Table II.

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TABLE II

STABILITY OF THE COMPLEX

Time elapsed	*Absorbancy*
0 h	0.680
1 h	0.682
2 h	0.680
3 h	0.682
17 h	0.664

It appears that the color is stable during at least three hours, a 17-hour waiting period giving a decrease of only 2.3%.

INFLUENCE OF THE pH

The influence of the pH on the complex formation was investigated from pH 1 to 8, using buffer solutions according to BRITTON[5]. The pH was measured before and after extraction with a Radiometer 22, using a glass electrode and a saturated calomel electrode. Results for solutions containing 10 μg Co/ml in 25 ml buffer are summarized in Table III.

TABLE III

INFLUENCE OF THE pH

Buffer	*pH* *before*	*after*	*Absorbancy*
NaAc + HCl	1.26	1.25	0.000
,,	1.44	1.44	0.000
,,	2.05	2.06	0.000
,,	2.47	2.60	0.050
,,	3.02	3.32	0.392
,,	3.40	3.75	0.544
NaAc + HAc	4.05	4.50	0.688
,,	5.00	5.40	0.675
,,	5.59	5.95	0.688
$NaOH + KH_2PO_4$	6.00	6.04	0.678
,,	6.46	6.48	0.682
,,	6.82	6.84	0.670
,,	7.02	7.03	0.668
,,	7.90	7.80	0.619

It appears that the complex formation is quantitative between pH 4 and 7, so the solution to be determined needs no accurate pH adjustment.

INFLUENCE OF THE REAGENT CONCENTRATION

The influence of the reagent concentration was investigated for concentrations of 0.0125, 0.025, 0.050, 0.075 and 0.1%, corresponding to a cobalt-reagent ratio of 1/5, 1/10, 1/20, 1/30 and 1/40. Results are summarized in Table IV.

TABLE IV

INFLUENCE OF THE REAGENT CONCENTRATION

Reagent concentration in %	*Absorbancy*
0.0125	0.674
0.025	0.680
0.050	0.680
0.075	0.687
0.100	0.684

It appears that the extraction is quantitative from a reagent concentration of 0.025% onwards.

CALIBRATION CURVE

Taking in account the optimum conditions for the cobalt determination previously investigated, the following procedure was adopted for the calibration curve:

Place in a separatory funnel 25 ml of a cobalt solution covering the range of 0.5 to 3 μg Co/ml, the pH being adjusted between 4 and 7 with a phosphate buffer. Extract successively with one 10 ml and two 5 ml portions isoamylalcohol containing 0.025 % isonitrosodimedon. Collect the organic phase in a 25 ml calibrated flask and dilute to the mark with ethanol. The absorbancy is measured versus a blank at 374 mμ with a Beckman DU spectrophotometer using 1 cm quartz cells. Results are summarized in Table V.

TABLE V

CALIBRATION CURVE

μg Co/ml	*Absorbancy*	*Absorbancy Index k*	*Δk*
0.50	0.165	0.330	—4
0.75	0.245	0.327	—7
1.00	0.332	0.332	—2
1.25	0.416	0.333	—1
1.50	0.498	0.332	—2
1.75	0.591	0.338	+4
2.00	0.678	0.339	+5
2.25	0.758	0.337	+3
2.50	0.840	0.336	+2
2.75	0.918	0.334	0
3.00	0.996	0.332	—2
		3.670	

It appears that Beer's law is followed at least up to 3 μg Co/ml, the mean deviation on the calibration curve being 1.1%.

TABLE VI

INFLUENCE OF FOREIGN IONS

	Foreign ion	*Absorbancy 2 μg Co/ml*	*Error*
Cations			
	Na^+	0.674	0.9
	K^+	0.676	1.2
	Ca^{+2}	0.672	0.6
	Mg^{+2}	0.673	0.75
	Zn^{+2}	0.668	0
	Cr^{+3}	0.836	25!
	Ni^{+2}	0.335	50!
	Fe^{+3}	—.—	dark blue
	Cu^{+2}	—.—	dark brown
Anions			
	PO_4^{-3}	0.668	0
	SO_3^{-2}	0.668	0
	CrO_4^{-2}	0.796	17.6!
	$S_2O_3^{-2}$	0.675	1.0
	VO_3^-	0.660	1.2
	MoO_4^{-2}	0.685	2.5
	F^-	0.687	2.8
	citrate	0.690	3.3
	oxalate	0.693	3.75
	tartrate	0.690	3.3

INFLUENCE OF FOREIGN IONS

To determine the selectivity of the cobalt determination, a series of foreign ions were examined in a 100 to 1 Co proportion. The cations were present as nitrates, whereas the sodium or potassium salts were used for the anions. Results are represented in Table VI.

From Table VI it appears that Fe^{+3}, Cu^{+2}, Cr^{+3} and Ni^{+2} disturb the cobalt determination in a 100-fold excess. Different methods were tried to mask these ions without success.

The absorption curves of the Fe^{+3}, Cu^{+2} and Ni^{+2} complexes were registered at concentrations of 16, 12 and 30 μg/ml, respectively (Fig. 2). It appears that the absorption curves present too great an analogy with the cobalt complex to avoid interference by choosing another wavelength for the absorbancy measurements.

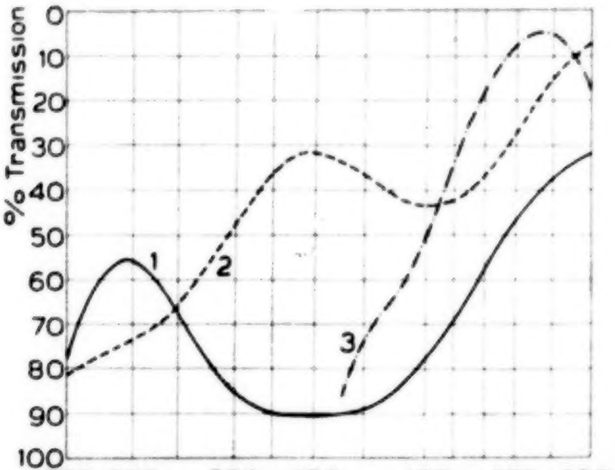

Fig. 2. Absorption curves: (1) Fe^{+3}; (2) Cu^{+2}; (3) Ni^{+3}.

SUMMARY

An extraction procedure with iso-amylalcohol for the determination of traces of cobalt was developed using isonitrosodimedon. At 374 mμ, the wavelength of maximal absorption, the molar extinction coefficient is as high as 19,680, allowing cobalt determination as low as 0.5 μg/ml in the organic phase. The extraction is quantitative between pH 4 and 7. The most common ions in a 100-fold excess do not disturb the determination, though Fe^{+3}, Cu^{+2}, Cr^{+3} and Ni^{+2} should be absent.

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SPECTROPHOTOMETRIC DETERMINATION OF GERMANIUM WITH PHENYLFLUORONE AFTER BENZYL ALCOHOL EXTRACTION

by

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INTRODUCTION

Since GILLIS, HOSTE AND CLAEYS[1] proposed phenylfluorone as a specific spot test for germanium, this reagent was adopted for the absorptiometric determination of traces of germanium by CLULEY[2]. As the phenylfluorone-germanium complex is insoluble in aqueous solution, it was found necessary to add a stabilizing agent to avoid precipitation. Distillation of the germanium as tetrachloride is recommended before the determination to avoid interference of some foreign ions. Extraction of the tetrachloride with carbon tetrachloride is also feasible[3].

STIPANITS AND HECHT[4] have attempted to increase the sensitivity of the reaction by liquid - liquid extraction of the complex. They were, however, unable to find a suitable organic solvent*.

It seemed, therefore, desirable to investigate the extractability of the germanium with a solvent immiscible with water. This procedure would stabilize the color and increase the sensitivity. It appeared that, of the large number of solvents investigated, only benzyl alcohol is suitable.

TRANSMITTANCY CURVE OF GERMANIUM–PHENYLFLUORONE IN BENZYL ALCOHOL

The transmittancy of the germanium complex was determined as a function of the wavelength from 550 to 400 mμ.

Procedure

Place in a separatory funnel 25 ml of a solution of 0.5*M* HCl containing 0.3 μg/ml Ge. Add 5 ml 0.03% phenylfluorone dissolved in a mixture of 95 ml ethanol + 5 ml H_2SO_4 (1 + 6). Wait at least 5 min and extract three times with 10 ml, 5 ml and 5 ml benzyl alcohol, resp., shaking each time for 3 min. This procedure extracts the complex as well as the reagent. The benzyl alcohol fractions are collected in a volumetric flask of 25 ml and diluted to the mark with ethanol. The transmittancy is measured, *versus* a blank, with a DR-Beckman Recording spectrophotometer in matched corex cells of 1 cm.

The results are represented in Fig. 1, curve 1. Curve 2 represents the transmittancy curve of 0.003% phenylfluorone *versus* benzyl alcohol as a blank. As will be shown later, the procedure used represents the optimum working conditions.

It appears that the phenylfluorone - germanium complex in benzyl alcohol has a quite narrow absorption band with a maximum at 505 mμ. At this wavelength the value of the absorbancy is 0.598, giving a molar extinction coefficient of 144,700.

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* While our investigation was in progress, KIMURA, SAITO AND ASADA[5] proposed dimethylaminophenylfluorone as a colorimetric reagent for germanium. As this reagent contains a basic group, the germanium complex is soluble in acid medium and the use of a stabilizing agent is also avoided.

Consequently, the sensitivity of the reaction is practically twice as high as in aqueous medium.

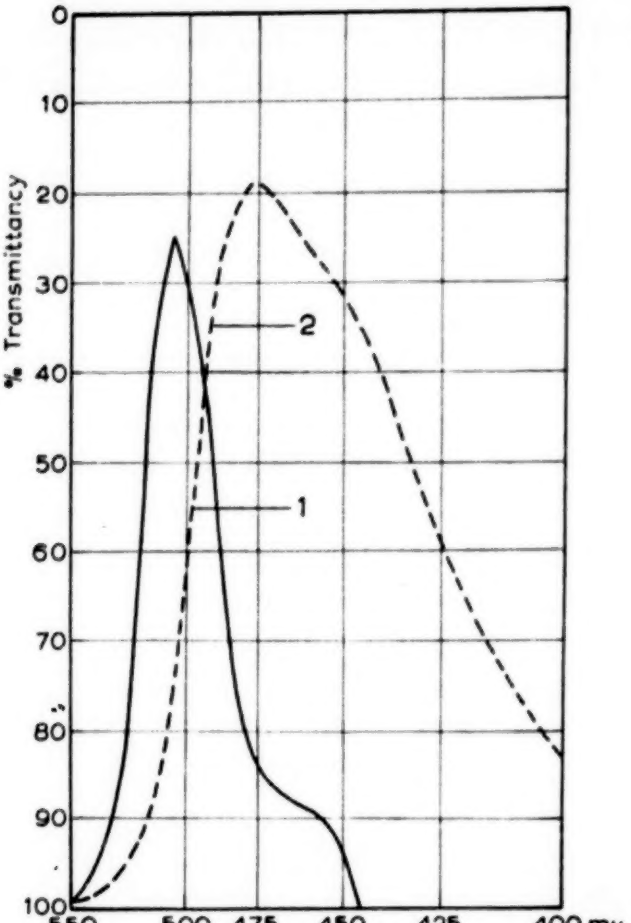

Fig. 1. Transmittancy curve of germanium–phenylfluorone in benzyl alcohol.

DISTRIBUTION COEFFICIENT OF THE COMPLEX

To determine the distribution coefficient of the complex, the procedure described above was used, restricting, however, the extraction to one 10 ml portion of benzyl alcohol. When a clear-cut separation of the two phases is obtained, the benzyl alcohol fraction is collected in a 25-ml volumetric flask, 2 ml ethanol are added and diluted to the mark with benzyl alcohol. The absorbancy of this solution had a value of 0.598, thus giving a quantitative extraction in one operation. The experiment shows that the distribution coefficient of the complex is too high to be determined accurately spectrophotometrically.

STABILITY OF THE COMPLEX

The absorbancy of a solution of the complex, prepared as described above, was measured during eight days. No change in the absorbancy could be found.

TIME INFLUENCE ON THE COLOR DEVELOPMENT

CLULEY stated that the complex formation depends on both reagent and acid concentration. In 1N HCl a waiting period of 30 min was necessary, for the reagent concentration considered. As shown in Table I, it is necessary to wait 5 min before extracting the complex to attain a maximum absorbancy.

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TABLE I

INFLUENCE OF THE WAITING TIME

Time in min	*Absorbancy*
0	0.556
5	0.598
10	0.597
30	0.598

INFLUENCE OF THE ACID CONCENTRATION

As germanium is either extracted or distilled as tetrachloride from a HCl solution, the only acid investigated was hydrochloric acid. Our results are summarized in Table II.

TABLE II

INFLUENCE OF THE HCl CONCENTRATION

HCl normality	*Absorbancy*
0.1	0.558
0.25	0.585
0.5	0.598
1.0	0.473
2.0	0.257

In all cases the extraction of the complex was carried out after a 30-min waiting period. It appears that a total 0.5*N* HCl concentration is optimal.

INFLUENCE OF THE PHENYLFLUORONE CONCENTRATION

To investigate the influence of the reagent concentration, solutions containing 0.015, 0.03, 0.045, 0.06 and 0.12% phenylfluorone were prepared by dissolving appropriate quantities in 95 parts of ethanol and 5 parts of H_2SO_4 (1+6). 25 ml of a solution were used, containing 0.5 μg Ge/ml in 0.5*N* HCl; 5 ml reagent are added. After 30 min, extraction with benzyl alcohol was carried out as already described. Absorbancies were measured at 505 mμ with a Beckman DU spectrophotometer using matched corex cells. Results are summarized in Table III.

TABLE III

INFLUENCE OF THE PHENYLFLUORONE CONCENTRATION

% Phenylfluorone	*Absorbancy*
0.015	0.961
0.03	0.982
0.045	0.805
0.06	0.691
0.12	0.273

Table III shows that the reagent concentration is rather critical, 5 ml 0.03% phenylfluorone giving the highest absorbancy. Higher concentrations of phenylfluorone cause not only a lowering of the absorbancy, but also change the whole of the absorption spectrum as can be seen from Fig. 2.

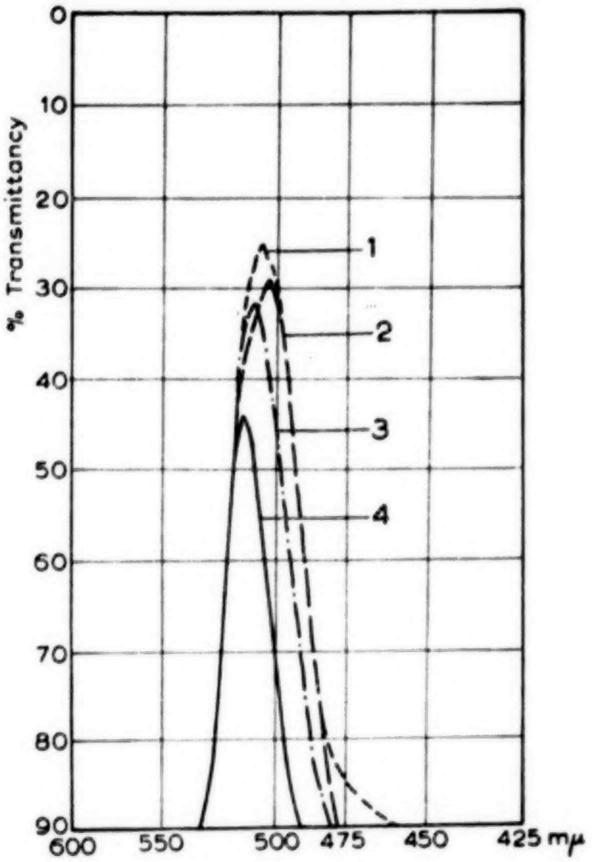

Fig. 2.
Curve 1: 0.03% phenylfluorone.
Curve 2: 0.015% phenylfluorone.
Curve 3: 0.06% phenylfluorone.
Curve 4: 0.12% phenylfluorone.

It was shown that the reagent itself does not follow Beer's law. In Fig. 3, curve 1 represents the absorption spectrum of 0.003% phenylfluorone in benzyl alcohol, measured in 1 cm cells with a Beckman DR recording spectrophotometer. Curve 2 represents the absorption spectrum of 0.15% phenylfluorone, measured with the same instrument, in a 0.1 cm cell *versus* 0.012% phenylfluorone solution in a 1 cm cell as reference. In this way the measured absorbancies should correspond to an absolute value of 0.003% of phenylfluorone. As can be seen from Fig. 3 there is a considerable discrepancy between the two curves. It is assumed that this is probably due to a dimerization of the phenylfluorone molecules, the associated molecules also giving rise to a germanium complex with different optical properties.

CALIBRATION CURVE

From the previous experiments it appears that the spectrophotometric determination of germanium with phenylfluorone after benzyl alcohol extraction is most sensitive in $0.5\,N$ HCl and a reagent concentration of 5 ml 0.03% for a 25-ml sample solution.

The formation of the complex is quantitative after 5 min. The distribution coefficient is sufficiently high to achieve quantitative extraction with one 10-ml portion

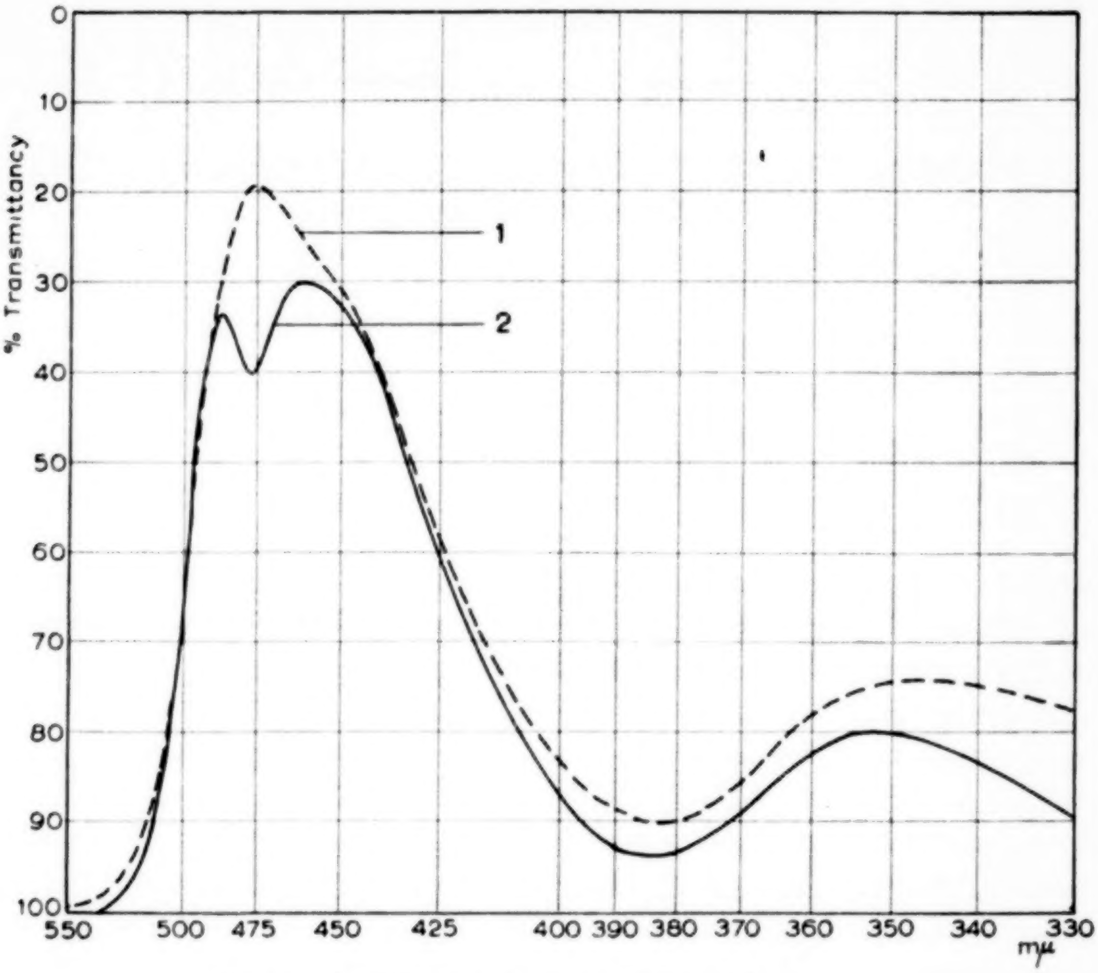

Fig. 3. Absorption spectrum of phenylfluorone.

of benzyl alcohol. It is, however, more practical to use more than one portion in order to avoid delay before a quantitative separation of both phases is achieved. As the benzyl alcohol phase tends to be cloudy, due to water droplets, ethanol is added before diluting to the mark. The addition of about 2 ml of ethanol does not change the absorption spectrum of the complex.

Procedure

Place in a separatory funnel 25 ml of a $0.5N$ HCl solution and amounts of germanium ranging from 0.05 to 0.5 μg germanium per ml. Add 5 ml reagent. Wait at least 5 min and extract successively with one 10-ml and two 5-ml portions of benzyl alcohol, shaking each time for 3 min. Collect the organic phase in a 25-ml calibrated flask and dilute to the mark with ethanol. The absorbancies are measured at 505 mμ *versus* a blank.

Reagents

(1) Hydrochloric acid, analytical grade.

(2) Standard stock solution of germanium: 0.7204 g pure ignited GeO_2 are fused in a platinum crucible with 2.5 g of sodium carbonate. The melt is dissolved in hot water and diluted to 500 ml. This solution contains 1 mg Ge/ml.

(3) Phenylfluorone solution: 0.030 g phenylfluorone are dissolved in a mixture of 85 ml ethanol + 5 ml H_2SO_4 (1 + 6) on a steam bath, and made up to 100 ml with ethanol.

Apparatus

(1) 1-cm matched corex cells.

(2) Beckman DU or DR spectrophotometer.

The results of typical measurements are shown in Table IV.

TABLE IV

μg Ge/ml	*Absorbancy*	*Absorbancy index (k)*	*Δk*
0.05	0.102	2.04	3
0.10	0.205	2.05	4
0.15	0.300	2.00	1
0.20	0.414	2.07	6
0.25	0.504	2.01	0
0.30	0.598	1.99	2
0.35	0.701	2.00	1
0.40	0.790	1.97	4
0.45	0.885	1.97	4
0.50	0.982	1.96	5

Accuracy

Table IV shows a small deviation from Beer's law. Even if the mean absorbancy index of 2.01 is accepted, the mean deviation σ is still only 1.7%.

INFLUENCE OF FOREIGN IONS

The study of the influence of foreign ions on the determination of germanium was restricted to Ti^{+4}, Sn^{+2}, As^{+3}, Sb^{+3}, Bi^{+3}, Mo^{+6} and Fe^{+3}. Ti^{+4} and As^{+3} do not interfere in a 100-fold excess, whereas Mo, Bi, Sb, Sn and Fe interfere. In the presence of these ions, separation of germanium by distillation or extraction as tetrachloride is necessary.

SUMMARY

A procedure has been developed for the determination of traces of germanium with phenylfluorone using benzyl alcohol extraction. The procedure is very sensitive, the molar extinction having a value of 144,700. The concentration of germanium in the organic phase should be between 0.05 and 0.5 μg/ml.

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A METHOD FOR THE DETERMINATION OF PHOSPHORUS IN ORGANIC COMPOUNDS

by

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Since its introduction by SUMNER[1], ferrous sulphate has been seldom used as a reductant in molybdenum blue methods. It was used by ROCKSTEIN AND HERRON[2] in solutions of high acidity to prevent interference by silicate. TAUSSKY AND SHORR[3] used it for the determination of phosphorus in biological specimens. Interfering substances and the effect of varying the concentrations of the reagents have been investigated by TAUSSKY AND SHORR, and by CHALMERS[4], who used ferrous ammonium sulphate as reductant.

Most organic phosphorus compounds are decomposed quantitatively to yield orthophosphoric acid when they are heated with sulphuric acid and either nitric acid or perhydrol to complete the oxidation. Difficult cases have been discussed by DAVIES AND DAVIES[5]. If the excess oxidant is removed by evaporation of the solution to fumes of sulphur trioxide there is an uncertainty about the amount of acid left. The object of this investigation was to determine ranges of concentration of the reagents that would permit the use of this method of decomposing the sample and of ferrous ammonium sulphate as reductant in the molybdenum blue reaction.

EXPERIMENTAL

10% w/v ammonium molybdate, 12.5% v/v sulphuric acid, and 10% w/v ferrous ammonium sulphate solutions were prepared. A little sulphuric acid was added to the ferrous ammonium sulphate. Aliquots of standard phosphate solution (100 µg phosphorus per ml) were transferred to a 100 ml calibrated flask, diluted to about 40 ml, and varying amounts of sulphuric acid, molybdate, and reductant were added to it in that order, the solution being mixed between additions. The solution was diluted to volume, mixed thoroughly, and the optical density measured spectrophotometrically in 1 cm cells at 750 mµ, against a blank containing the reagents only. A plot of optical density against time gave the rate of colour development.

It was found that the important factors were the concentration of the reductant and the ratio of the concentrations of the acid and molybdate. Temperature changes had a small effect on the rate of colour development, but could be neglected if they did not exceed a few degrees. If the acid/molybdate ratio was too low, reduction of the blank occurred. If it was too high, the rate of colour development was decreased in the early stages. For a given concentration of molybdate, a range of concentration of acid could be found which gave an almost unvarying rate of colour development. Increase in the concentration of reductant increased the rate of colour development. The colour developed rapidly in the first 5 to 15 min (depending on the acid/molybdate ratio), then increased slowly but uniformly for several days. At the end of this period the colour continued to increase linearly with time but at a reduced rate, until eventually reduction ceased. After the first rapid reaction, the rate of colour development was so low that the optical density, measured during a time range of about 5 min, appeared to be constant within the limits of precision associated with the measuring instrument. Both of the slow rates of reaction appeared to be directly proportional to the phosphate concentration. A plot of optical density (measured after 15 min) against phosphate concentration was found to be reproducible but showed that Beer's law was not obeyed; if, however, the optical densities were corrected for the presence of the second slow reaction, a linear plot was obtained. This was assumed to imply that both slow reactions were going on simultaneously. The mechanism of the reduction is being made the subject of a separate investigation.

In the decomposition of the sample it was found that to ensure complete removal of nitric acid it was necessary to evaporate to fumes of sulphur trioxide, cool, add a little water to decompose any nitrosyl sulphuric acid, and evaporate to fumes again.

METHOD

Reagents

All reagents should be of recognised analytical quality.

Acid molybdate solution. Dissolve 100 g of ammonium molybdate in 1 l of water and add with stirring to a cold solution of 250 ml of concentrated sulphuric acid in 700 ml of water. Dilute to 2 l. The solution keeps indefinitely.

Ferrous ammonium sulphate solution. A 10% solution containing 1–2 ml of 4*N* sulphuric acid to prevent any hydrolysis. The solution must be prepared on the day it is to be used.

Sulphuric acid. Add 125 ml of concentrated sulphuric acid to 800 ml of water, cool, and dilute to 1 l.

Procedure

With the aid of a long-handled weighing stick, weigh a 3 to 10 mg sample into a small Kjeldahl flask (bulb capacity 15 ml), add 1 ml of concentrated sulphuric acid and a few drops of concentrated nitric acid, and heat over a micro-bunsen flame in the usual Kjeldahl fume-extraction apparatus to decompose the sample. Evaporate to fumes of sulphur trioxide, cool the flask, wash down the neck with 1–2 ml of water, and evaporate to fumes again. Cool, wash down the inside of the flask with 4–5 ml of water and transfer the contents of the flask to a 100 ml calibrated flask, using four 5-ml portions of water for rinsing. Add 20 ml of the acid molybdate solution and 10 ml of the ferrous ammonium sulphate solution, rinsing the neck of the flask and mixing the solution between additions. Dilute to the mark, mix thoroughly, allow to stand for 15 min and measure the optical density at 750 mμ in 1 cm cells in a spectrophotometer, compared with a blank containing the reagents and prepared in the same way as the samples.

Calibration curve

Dissolve 4.394 g of dried potassium dihydrogen phosphate in water and dilute accurately to 1 l. This stock solution contains 1 mg of phosphorus per ml. Dilute it tenfold to obtain a stock solution containing 100 μg of phosphorus per ml. Make all solutions about 0.001–0.005*N* in sulphuric acid to prevent adsorption of phosphate on the glass. Transfer suitable aliquots of standard solution to 100 ml calibrated flasks, add 8 ml of the diluted sulphuric acid (equivalent to 1 ml of the concentrated acid), 20 ml of the acid molybdate, and 10 ml of ferrous ammonium sulphate solution, and proceed as described above. A variation of 3 ml in the amount of diluted acid causes an error of not more than 5 parts per 1000. The curve should cover the range 0–1600 μg of phosphorus per 100 ml.

RESULTS

A number of standard samples were analysed by the method given. The results are presented in Table I. The method is rapid — four batches were completed in an afternoon's work of 3½ hours — and is sufficiently accurate for normal purposes. The main feature of interest, however, is the apparent existence of two reactions proceeding simultaneously. The reduction method is not suitable for determination of hydrolysis rates of phosphate esters because of the high acidity used. Two decimals are quoted in most of the results for statistical purposes only.

TABLE I

Sample	*P by this method* %			*Mean P* %	*P content* %
Potassium dihydrogen phosphate	23.3	22.9	22.7		
	22.7	22.9	22.1	22.8	22.8
	22.7	23.1			
Glucose-1-phosphate	8.18	8.04	8.31		
	8.13	7.99	8.18	8.12	8.32
	8.00	8.03	8.19		
Quinine hypophosphite	7.33	7.33	7.18		
	7.61	7.55	7.50	7.35	7.26
	7.41	6.97	7.37		
	7.28				
Triphenylphosphate	9.55	9.62	9.77		
	9.53	9.74	9.65	9.58	9.53
	9.56	9.64	9.40		
	9.36	9.71			
Triphenylphosphine	11.82	11.36	11.74		
	11.77	11.68	11.78	11.66	11.81
	11.44	11.64	12.01		
	11.42	11.55			

SUMMARY

The sample is decomposed by heating with nitric and sulphuric acids, the nitric acid is completely removed, and phosphomolybdic acid is formed under carefully controlled conditions of acidity and reduced to molybdenum blue by means of ferrous ammonium sulphate. The colour intensity is measured spectrophotometrically.

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THE SPECTROPHOTOMETRIC DETERMINATION OF COPPER AS THE 2-FUROYLTRIFLUOROACETONE CHELATE

by

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INTRODUCTION

Several β-diketones have been studied in this laboratory to determine their potential use as analytical reagents. McINTYRE *et al.*,[1,2] observed in these studies that several of the β-diketones, 2-furoyltrifluoroacetone and 2-thenoyltrifluoroacetone, reacted quantitatively with the cupric ion to form a stable chelate that was insoluble in water but soluble in some organic solvents. Organic extracts of the copper chelate were an intense green. Of 43 common metal ions studied, only the cupric, cuprous, and nickel ions formed a green chelate. The nickel chelates absorbed light at approximately the same wavelength as the copper, but their extinction coefficients were much larger. As a result of these observations, a spectrophotometric method for the determination of copper was developed using 2-furoyltrifluoroacetone. The sulfur analog, 2-thenoyltrifluoroacetone, behaves in almost an identical fashion as the furan derivative. Absorption spectra of some heavy metal chelates of 2-thenoyltrifluoroacetone in absolute ethyl alcohol were determined by BERG AND McINTYRE[1]. These spectra indicate that if the thenoyl derivative were used in the same procedure, than an even more selective analysis might be the result.

APPARATUS AND REAGENTS

2-Furoyltrifluoroacetone (Midcontinent Chemical Co.) was used as a 5 weight% solution of the reagent in ethyl alcohol.

A standard copper solution was prepared by dissolving 1.0000 g of pure copper foil in a minimum of nitric acid and diluting to 500.0 ml.

Test solutions of metal ions were prepared from reagent grade chemicals as a 1 weight% solution of the metal. Nitrate salts were used when available.

A Beckman Model DU spectrophotometer with matched 1.000-cm quartz cells and temperature controlled cell housing was used for all optical measurements.

Methyl isobutyl ketone, reagent grade, was used as the organic extracting solvent.

Thorn Smith analyzed brass samples were used for checking the accuracy of the method.

All other chemicals used were reagent grade.

PROCEDURE

Standard procedures were worked out that gave consistently good results for the determination of copper in synthetic standards and in various brasses. Weighed samples were dissolved in a minimum of nitric acid and diluted to a known volume in volumetric flasks. Aliquots, containing from 1 to 10 mg of copper were taken from the synthetic and brass sample solutions and added directly to small separatory funnels. Five to ten ml of saturated sodium acetate solution were added to each sample. The sample solution was diluted to about 40 ml with distilled water and the pH was adjusted to about 7 with sodium hydroxide solution. Two ml of the 5 weight% solution of 2-furoyltrifluoroacetone in ethyl alcohol were added. The samples were shaken vigorously for a few seconds and then left to stand for several minutes. Five ml of methyl isobutyl ketone were added to each sample and the samples were gently mixed. The lower aqueous phase was drained off and tested for completeness of precipitation by adding several drops of the β-diketone reagent and then re-extracted with 3 ml of fresh ketone. The organic phases were combined in a volumetric flask and diluted to 10.0 ml with pure solvent. The per cent transmission of the green organic phase was measured at 660 mμ in 1.000-cm quartz cells on the Beckman DU spectrophotometer using a blank of pure methyl isobutyl ketone.

A standard working curve for copper was established by plotting the per cent absorbancy versus the concentration of copper in the synthetic standard copper samples. The weight of copper in the brass samples was established by comparing the per cent absorbancy of these samples to the standard curve for copper.

The effect of possible interfering ions on the procedure was established by adding known amounts of the foreign ions to the sample aliquots and comparing the per cent absorbancy of the organic extract to that of a pure copper standard.

RESULTS AND DISCUSSION

In the course of these studies it was shown that from 1 to 10 mg of copper as the 2-furoyltrifluoroacetone chelate were quantitatively extracted from less than 200 ml of water into 5 ml of methyl isobutyl ketone with a single extraction. In practice, two extractions were effected to remove the tedium associated with completely separating the organic and aqueous phases. A small amount of the organic phase lost at the interface in the first extraction was readily recovered in the second extraction. The organic phase was so dilute with copper on the second extraction that the loss of one or two drops of this phase was not critical.

The absorption spectrum for the copper(II) chelate of 2-furoyltrifluoroacetone in methyl isobutyl ketone is given in Fig. 1. The color system does not obey Beer's Law at the higher concentrations but there is no shift in the wavelength of maximum absorption over the acceptable working range of concentrations.

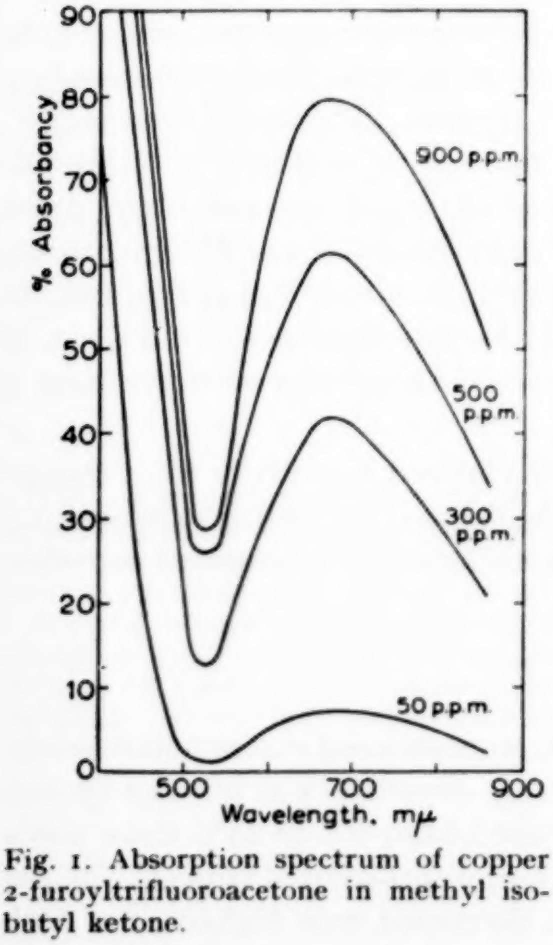

Fig. 1. Absorption spectrum of copper 2-furoyltrifluoroacetone in methyl isobutyl ketone.

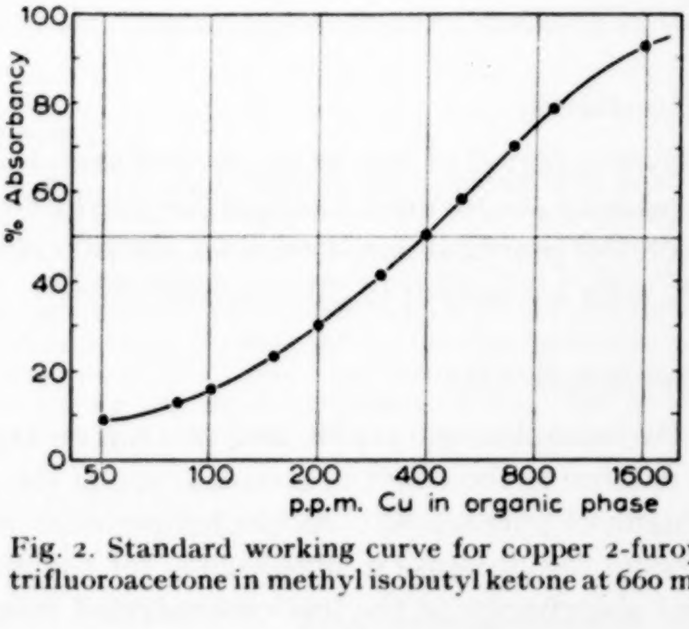

Fig. 2. Standard working curve for copper 2-furoyltrifluoroacetone in methyl isobutyl ketone at 660 mμ.

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Fig. 2 is the standard working curve for the system. The Ringbom plot shows that the satisfactory working range for the system is approximately 100 to 1000 p.p.m. copper in the organic extract. This low sensitivity for the color measurement is misleading because the actual amounts of copper involved ranged from 1 to 10 mg. When it is considered that a single extraction step will quantitatively remove 1 mg of copper from less than 200 ml of sample solution, the method is fairly sensitive.

Analysis results

Brass samples containing varying amounts of copper, lead, tin, zinc, and elements usually reported as mixed oxides, were dissolved in a minimum of nitric acid. No pretreatment, other than dissolution, of samples prior to the outlined procedure was necessary. Metastannic acid precipitates were ignored and offered no problem in the subsequent reaction and extraction of copper. The results of multiple analyses on five different brasses and seven synthetic copper samples are given in Table I. The brass samples were determined with a 1.0% average relative error. The average relative error for the synthetic samples was 0.91%.

TABLE I

RESULTS OF COPPER ANALYSES ON BRASS AND SYNTHETIC STANDARDS

Brass sample No.	*Copper taken mg*	*Copper found mg*
1	4.372	4.42
2	4.108	4.07
3	4.430	4.48
4	4.924	4.99
5	3.924	3.90
Synthetic sample No.		
1	1.00	0.98
2	1.50	1.48
3	3.00	2.97
4	5.00	4.95
5	6.00	5.95
6	7.00	7.00
7	9.00	8.90

Color stability

Over a period of one week, several samples were checked repeatedly for a change in per cent absorbancy. Changes observed were negligible and well within experimental error. For practical purposes, then, the per cent absorbancy may be measured immediately after extraction or after several days.

Temperature effect

Two samples, 300 p.p.m. and 900 p.p.m. copper, were investigated simultaneously to determine the effect of temperature on the per cent absorbancy at 660 mμ against a blank of pure solvent. As the temperature was raised from 8°C to 24°C there was a pronounced decrease in absorbancy for the greater concentration of copper. The per cent absorbancy of the less concentrated solution decreased only slightly. For both concentrations, the per cent absorbancy was constant from 24°C to 40°C. Since room temperatures varied from 24°C to 28°C, temperatures were not controlled for the spectrophotometric measurements. For room temperatures below 24°C, it would be necessary to control the temperature for all spectrophotometric work.

Diverse ion effect

Absorption spectra of some of the heavy metal β-diketone chelates in absolute ethyl alcohol[2] suggested that this procedure would be fairly specific for the determination of copper. Diverse ions in known amounts were added to aliquots of the standard synthetic and brass samples. Copper was precipitated and extracted as the chelate.

TABLE II

EFFECT OF DIVERSE IONS ON THE ABSOLUTE % ABSORBANCY OF STANDARD COPPER SAMPLES

Interference	*Concentration ratio of interference to copper*	*Δ absolute % A*
Fe^{+3}	0.45	1.5
Co^{+2}	2.9	0.1
Ni^{+2}	1.7	1.0
Mn^{+2}	2.1	0.5
Ce^{+4}	2.6	17.7
Pd^{+2}	4.1	2.8
V^{+3}	2.3	3.4
* Zn^{+2}, Cd^{+2}, Hg^{+2}, Sn^{+2}	10	—1.2

* Concentration ratio of each metal in mixture to copper is 2.5.

Table II shows the effect that definite quantities of diverse ions have on the absorbancy of the extracted copper solutions. Only iron(III), nickel(II), cerium(IV), palladium(II), and vanadium(III), are serious interferences among the common metals.

Mercury(II), lead(II), zinc(II), cadmium(II), beryllium(II), aluminum(III), gallium(III), indium(III), lanthanum(III), thorium(IV), zirconium(IV), and the alkaline earth metals form white precipitates with the diketone, but either do not extract into the organic solvent or do not absorb light at 660 mμ. The effect of these ions was illustrated by the fact that a mixture of zinc(II), cadmium(II), mercury(II), and tin(II) ions, each at a concentration of 2½ times the copper concentration, resulted in only a small negative interference.

SUMMARY

The copper 2-furoyltrifluoroacetone chelate may be quantitatively precipitated from aqueous solutions and extracted into organic solvents. The organic extract, which is an intense green, absorbs light strongly at a wavelength of 660 mμ. Although the β-diketone is not a specific reagent, most of the other metal chelates are colorless, not extracted, or do not absorb light at 660 mμ.

A rapid, sensitive, and reasonably specific spectrophotometric method for the determination of copper was developed on these properties. The method is applicable to the determination of as little as one mg of copper at concentrations as low as 5 p.p.m. Iron, vanadium, cerium, nickel, and palladium are the only serious interferences among the more common elements. The method appears suited for the determination of copper in brass samples and in aluminum based alloys.

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THE DETERMINATION OF RUBIDIUM BY THE METHOD OF STABLE ISOTOPE DILUTION

by

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INTRODUCTION

In the method of isotope dilution the quantity of an element present in a sample is estimated from the change it produces in the isotopic composition of a known quantity of an isotopically enriched tracer of the element. This method, which has recently been used for rubidium determinations by several groups of workers[1-5], was used for the determinations described in this paper partly so that the results obtained could be compared with those found independently at Harwell by neutron activation analysis, and partly in preparation for a limited programme of geological age determination by the rubidium-strontium method.

Neutron activation analysis[6,7] and flame photometry[8] are two other methods used recently for rubidium determinations. In these methods the final measurement, that is counting the rubidium activity induced by neutron irradiation or measuring the intensity of the flame spectrum of rubidium, needs less time than a mass spectrometric determination of the rubidium isotope ratio, but the requirements for the chemical treatment of the sample are much more stringent. For neutron activation analysis the final product must be both chemically and radiochemically pure and in a stoichiometric form, and for flame photometric determinations the rubidium must be separated from elements that cause interference; this may mean that the chemical treatment extends over a period of several days. In isotope dilution analysis interference may occur only between elements with isobars; for rubidium this means strontium, which does not ionise under the mass spectrometric conditions used for producing rubidium ions. As a result of this and the high sensitivity of the mass spectrometer for rubidium, the chemical treatment may be restricted to that necessary to decompose the sample and to establish that the tracer element and that in the sample are in the same chemical form.

EXPERIMENTAL

Mass spectrometry

Isotope ratios were determined with a 6" radius 60° sector mass spectrometer equipped with a surface ionisation solid source and a conventional detector system of a Type 954 electrometer valve and a d.c. amplifier. Before they were used for the analysis of samples, the filament units were cleaned with cold concentrated hydrochloric acid and demineralised water, fitted with clean nickel "flags" if required, and decontaminated by running them at a high filament temperature in the mass spectrometer.

Rubidium may be ionised in two ways: rubidium nitrate may be used with a lithium type ion source[9,10] or rubidium sulphate may be placed directly on the tungsten filament. In the first type the sample is placed on a nickel "flag", mounted about 2 mm away from the tungsten filament, and is volatilised by radiant heat. A sample containing about 1 μg is adequate for this method of mass spectrometric analysis, and the determination may be combined with one for lithium. However, when an analysis is made in this way, the ion source can easily become contaminated with rubidium and cause "memory effects" in subsequent analyses. To avoid this source of error, the ion box was fitted with a platinum lining which could be removed and cleaned in boiling nitric acid before each analysis. The second method of analysis, where the sample is placed directly on the tungsten filament, is much more sensitive and a determination may be made with 0.001–0.01 μg of rubidium.

The side filament technique was used for most of the measurements for the rock samples to permit both the rubidium and the lithium contents to be determined[11]. Centre filament loading was used for the analysis of the sea-water samples, where it enabled the separation of rubidium from other salts present to be avoided, and it was also used to check the results obtained for the rock samples by the side filament method.

Chemical procedures

Rock samples. For each determination a portion of G-1 or W-1 was weighed into a platinum crucible in which a measured quantity of the tracer solution had previously been taken to dryness. The rock sample was attacked with a mixture of hydrofluoric and perchloric acids, taken to dryness, and the residue heated at 500–520°C, for at this temperature iron and aluminium perchlorates decompose to oxides, and the alkali metal perchlorates are converted to chlorides. The residue left by this thermal decomposition was heated with demineralised water to yield an aqueous extract containing the alkali metals. This solution was heated to dryness, and its residue was taken to dryness twice with concentrated nitric acid; a little demineralised water was then added and a portion of the solution transferred to the nickel flag of a mass spectrometer ion source. This method of acid attack has been used previously for rubidium determinations[2,3,4,5], and a detailed description of the method used for this work has been given elsewhere[11]. For both rock samples a determination was also made by the centre filament method. The residue left after removing a sample for a side filament determination was treated with a few drops of concentrated sulphuric acid and heated to dryness over a Meker burner. A portion of the aqueous extract was placed on the tungsten filament of an ion source.

Sea-water. Aliquots of the tracer solution were mixed thoroughly with measured volumes of sea-water in polythene bottles. In each case a small portion of the mixture was acidified with sulphuric acid and heated to dryness in a platinum crucible. A little of the aqueous extract of the residue was dried on the tungsten filament of a mass spectrometer source unit, and the rubidium isotope ratio determined. The quantity of solid sample used for each mass spectrometric analysis was approximately 0.1–1 mg and contained 0.001–0.01 μg of rubidium.

Calibration of tracer solution. The tracer was obtained as rubidium chloride and had the following isotopic composition:

$$^{85}\text{Rb}\ 15.0_5\%;\ ^{87}\text{Rb}\ 84.9_5\%$$

About 4 mg were dissolved in water, a few drops of concentrated hydrochloric acid added and the solution made up to 1 l.

The concentration of the tracer solution was determined by isotope dilution with normal rubidium. About 500 mg of Johnson, Matthey's "Specpure" rudibium chloride were dried at 180°C, weighed accurately, dissolved in water and made up to 500 ml. 1 ml of this solution was diluted to 500 ml with demineralised water containing a few drops of concentrated hydrochloric acid. 1 ml or 2 ml aliquots of this dilute standard were mixed in platinum crucibles with 1 ml or 2 ml aliquots of the tracer solution and the mixtures taken to dryness with nitric acid. Each residue was dissolved in a little water and transferred to the nickel "flag" of a mass spectrometer source unit.

In a second calibration a dilute standard was prepared as above, and similar aliquots of standard and tracer solutions were mixed in platinum crucibles and treated with sulphuric acid. The residues were transferred to the tungsten filaments of a set of source units.

This calibration procedure was recommended by INGHRAM[12] and SCHUMACHER[4] in order to ensure that the results obtained for samples should be free from the effects of mass spectrometric discrimination. It also obviates the need for a knowledge of the chemical purity of the tracer.

Contamination. For each set of estimates of the rubidium content of a sample, a value for a blank correction was determined by treating a portion of the tracer with the same quantities of the reagents as those used for the mixtures of tracer and sample. The blank corrections were not significant but the uncertainty in the determination of the isotope ratio was equivalent to an upper limit of ¼% of the quantity of tracer used, or 0.1–0.5% of the rubidium measured.

RESULTS

Evaluation of results

Results were calculated with the following formula:

$$x = y \frac{R_M - R_T}{R_N - R_M} \cdot \frac{85\, R_N + 87}{85\, R_T + 87}$$

where R_N is the ^{85}Rb/^{87}Rb ratio for the normal element
R_T is the ^{85}Rb/^{87}Rb ratio for the tracer element
R_M is the ^{85}Rb/^{87}Rb ratio for the mixture
y is the weight of tracer rubidium added
x is the weight of rubidium in the sample

Calibration of tracer solution

The values found for the concentration of the tracer solution are listed in Table I; both methods of ionisation were used.

TABLE I

THE DETERMINATION OF THE CONCENTRATION OF THE TRACER SOLUTION

Side "flag" calibration		*Centre filament calibration*	
Values found for the concentration μg/ml	*Mean value and standard deviation*	*Values found for the concentration μg/ml*	*Mean value and standard deviation*
2.566	$2.58_3 \pm 0.02$	2.59	2.62 ± 0.05
2.566		2.60	
2.592		2.68	
2.606			

Rubidium content of sea-water

Table II records the values found for the rubidium content of a sample of North Atlantic sea-water (49° 02′N, 15° 19′W) taken from a depth of 4000 metres. The mean value of 121.4 μg/l confirms the value of 120 ± 10 μg/l found by SMALES AND SALMON by neutron activation analysis[6], a result which is lower by a factor of almost 2 than previously reported values.

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TABLE II

THE RUBIDIUM CONTENT OF SEA-WATER

Volume of tracer solution (2.62 μg/ml)	*Volume of sea-water*	*Rubidium content μg/l*	*Mean value and standard deviation*
2 ml	10 ml	121.7	
2 ml	30 ml	121.0	121.4 ± 1.1
1 ml	20 ml	120.1	
1 ml	20 ml	122.6	

Rubidium contents of G-1 and W-1

The rubidium content of G-1 was determined by both the side filament and the centre filament methods.

TABLE III

THE RUBIDIUM CONTENT OF THE STANDARD GRANITE G-1

Side "flag" technique			*Centre filament technique*		
Mass sample mg	*Rubidium found p.p.m.*	*Mean value and standard deviation*	*Mass sample mg*	*Rubidium found p.p.m.*	*Mean value and standard deviation*
525.3	213		364.7	209	
631.6	214	214.8 ± 2.4	126.8	211	212.3 ± 3.2
376.4	214		202.9	215	
691.5	218		91.8	215	

The rubidium content of W-1 was determined on three occasions. For the second determination the samples were analysed by both the side and centre filament techniques. In view of the disagreement with the result reported by HERZOG AND PINSON[3] a third determination was made with a sample of W-1 obtained from The Department of Geology, Oxford, so that the possibility of sample inhomogeneity could be eliminated. These results are recorded in Table IV. Table V shows the values obtained by various methods of analysis for G-1 and for W-1.

CONCLUSIONS

The method of stable isotope dilution has been applied to the determination of the rubidium contents of two rock samples and sea-water. The results obtained are: G-1, 214 p.p.m.; W-1, 21.3 p.p.m.; sea-water, 121.4 μg/l. After considering the sources of uncertainty in the determination it seems likely that these values lie at least within ± 5% of the true value, and they agree with values obtained for these materials at Harwell by neutron activation analysis to within 3%.

The isotope ratio of rubidium may be determined in a mass spectrometer by either a side filament or a centre filament technique. The former method enables rubidium and lithium determinations to be combined; when the second method is used the results for sea-water suggest that it should be possible to determine quantities of the order of 1 p.p.m. in a sample as small as 1 mg with a chemical treatment involving little more than the decomposition of the sample. For both methods the coefficient of variation for four results is usually ± 1–2%.

TABLE IV

THE RUBIDIUM CONTENT OF THE STANDARD DIABASE W-1

Determination 1			*Determination 2*					*Determination 3*		
Side filament			*Side filament*			*Centre filament*		*Side filament*		
Mass sample mg	*Rb found p.p.m.*	*Mean value and standard dev'n*	*Mass sample mg*	*Rb found p.p.m.*	*Mean value and standard dev'n*	*Rb found p.p.m.*	*Mean value and standard dev'n*	*Mass sample mg*	*Rb found p.p.m.*	*Mean value and standard dev'n*
209.0	20.5_5		359.5	21.0_5		21.0_5		446.8	20.9	
265.0	21.4_5	21.4 ±0.7	562.9	21.2	21.2_1 ±0.13	21.6	21.4_4 ±0.25	159.6	21.0	21.0_7 ±0.18
95.9	21.4_5		554.7	21.2_5		21.5_5		241.9	21.1	
108.0	22.2_5		488.2	21.3_5		21.5_5		98.8	21.3	

TABLE V

THE DETERMINATION OF RUBIDIUM IN GRANITE (G-1) AND DIABASE (W-1) BY DIFFERENT METHODS

Analyst	*Method*	*Rubidium found p.p.m.*	
		G-1	*W-1*
Present method	Stable isotope dilution	214	21.3
Cabell and Smales[7]	Neutron activation analysis	219	21.3
Herzog and Pinson[3]	Stable isotope dilution	216	28.5
Horstman[8]	Flame photometry	205 204	19 25

SUMMARY

The rubidium contents of a granite (G-1), a diabase (W-1) and sea-water have been determined by mass spectrometric isotope dilution analysis. The values found are: G-1, 214 p.p.m.; W-1, 21.3 p.p.m.; sea water, 121.4 μg/l. These results show excellent agreement with values obtained at Harwell by neutron activation analysis, and the coefficient of variation for four determinations is usually ± 1-2%.

Rubidium ions were produced in the mass spectrometer by either a side filament or a centre filament technique. The former method enables rubidium and lithium determinations to be combined; the results obtained by the second method suggest that concentrations of the order of 1 p.p.m. may be determined for a sample of only a few mg with little chemical treatment beyond that required to decompose the sample.

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THE DETERMINATION OF LITHIUM IN ROCKS BY THE METHOD OF STABLE ISOTOPE DILUTION

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INTRODUCTION

The need for a precise and accurate method of analysis for trace quantities of lithium in rocks is illustrated by the values that have been reported for the lithium content of the standard diabase W-1; these range from 9 p.p.m. to 20 p.p.m. The analytical methods that have been used previously are emission spectrography and flame photometry. Both of these methods can be rapid and sensitive, but it is desirable to have an alternative and completely independent method, particularly for samples such as G-1 and W-1 that are used as standards[1,2]. Neutron activation analysis has been used for the determination of lithium isotope ratios both by triton counting[3] and by nuclear emulsion techniques[4], and the second of these methods has been applied to the determination of lithium in solids[5], but for concentrations of the order of 10 p.p.m. the accuracy is only 10–20%. Also the ^{7}Li/^{6}Li isotope ratio is not constant in nature but ranges from 12.3 to 12.9[6,7], and as neutron activation analysis yields only the concentration of the ^{6}Li isotope, this can introduce an error of 2–3%.

The method of stable isotope dilution should be capable of precise and accurate analyses for lithium. The quantity of lithium present is estimated from the change it produces in the isotopic composition of a known quantity of nearly isotopically pure lithium 6 or lithium 7. Once the tracer has been mixed thoroughly with the lithium in the sample the result obtained should be independent of the quantity of the lithium extracted for the isotopic analysis, so no errors are caused by adsorption losses on precipitates, etc. The mass spectrometric analysis can be made in the presence of a large excess of sodium and potassium, for there are no interference effects analagous to those that limit the accuracy of flame photometry and emission spectrography.

If only a part of the lithium is extracted, isotopic fractionation in the chemical treatment could be a possible source of error. Such an effect has been reported[6,8,9] and is especially bad for partial precipitations of lithium where it can cause changes in the ^{7}Li/^{6}Li isotope ratio of several percent. The presence of this type of error may be detected by the determination of the lithium content of a sample by isotope dilution with both lithium 6 and lithium 7. Any systematic fractionation or uncorrected mass discrimination would cause a high result to be obtained with one tracer and a low one with the other.

EXPERIMENTAL

Chemical treatment of the samples

In the chemical treatment it is necessary to establish that the tracer and the lithium in the sample are in the same chemical form, and to minimise the introduction of lithium contamination both from the reagents and from the atmosphere. If a solid reagent is used, it is difficult to make a valid "blank correction", so sinters and fluxes were avoided and the samples were decomposed with hydrofluoric acid. This method has been used in several recent determinations of the alkali metals[11,12,13], and after a flame photometric investigation of the decomposition of various silicate ores of lithium, both by hydrofluoric acid and by the Lawrence-Smith sintering method, SYKES[14] concluded that the former method of attack was preferable. In a mass spectrometer lithium is usually analysed in the form of lithium nitrate, rather than as the less volatile lithium sulphate, and consequently the samples were decomposed with a mixture of hydrofluoric and perchloric acids instead of the more commonly used one of hydrofluoric and sulphuric acids. The samples were heated with the acid under infra-red lamps, for direct heating on a hot plate tended to cause spraying and loss of tracer before the sample had been decomposed. The residue of perchlorates was heated in a furnace at 500–520°C so that the alkali metal perchlorates were converted to chlorides, and those of iron and aluminium to oxides. The alkali metal chlorides were extracted by treating this residue with boiling water, and the extract was taken to dryness with nitric acid. It was not found necessary to concentrate the lithium any further.

The quantity of lithium arising from the reagents was estimated by treating a sample of lithium tracer with the same quantities of the reagents. These "blank corrections" were about 1–2% of the quantity of lithium measured. Air borne contamination was limited by carrying out most of the operations in platinum crucibles covered by silica watch glasses or platinum lids.

Calibration of the tracer solutions

The lithium 6 and lithium 7 tracers were obtained in the form of lithium sulphate. They were dissolved in water, a few drops of concentrated hydrochloric acid were added, and the solutions were diluted to concentrations of approximately 2 μg/ml and 5 μg/ml respectively. The tracers had the following isotopic compositions:

Lithium 6:	^{6}Li 99.6%	^{7}Li 0.4%
Lithium 7:	^{6}Li 0.05%	^{7}Li 99.95%

The concentrations of the tracer solutions were determined by isotope dilution with normal lithium. A solution was prepared from about 1 g of Johnson, Matthey's "Specpure" lithium carbonate and standardised gravimetrically as lithium sulphate. A portion of this solution was diluted exactly to yield a standard solution with a concentration comparable with that of the tracer. Aliquots of the solutions of the normal and tracer element, measured either by volume or by weight, were mixed in platinum crucibles, and to each was added an aliquot of a solution of barium nitrate to give about a ten molar excess. Lithium sulphate is too involatile to be used directly in a mass spectrometer but lithium ion beams could be obtained very readily from this mixture. A blank correction was determined by mixing aliquots of the solutions of the tracer and the barium nitrate. In one case the correction was $5 \cdot 10^{-8}$ g lithium, and in another, with a smaller quantity of a more carefully prepared solution of barium nitrate, it was $3 \cdot 10^{-10}$ g lithium. These quantities were approximately 0.2% and 0.03% respectively of the quantity of lithium measured.

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The concentration of the tracer solution may be calculated from the measured isotope ratio and the known quantity of the normal element. This calibration procedure has been adopted in order to eliminate mass spectrometric discrimination[15]; a further advantage is that a knowledge of the chemical purity of the tracer is not required.

Mass spectrometric measurements

Isotope ratios were determined with a 6″ radius 60° sector mass spectrometer equipped with a surface ionisation solid source and a conventional detector system of a Type 954 electrometer valve and a d.c. amplifier. To avoid "memory" effects the ion box was fitted with a platinum lining which could be removed and cleaned before each analysis. The sample containing the lithium was placed on a nickel "flag" mounted about 2 mm away from the tungsten filament[16,17]. Those obtained from the rock samples were somewhat bulky, of the order of several milligrams, but stable lithium ion beams could be obtained if the filament temperature was raised slowly.

The filament units were similar to those used with the Metropolitan-Vickers Type M.S.5 mass spectrometer[10]. The tungsten filament and the kovar stems were cleaned in cold concentrated hydrochloric acid and demineralised water, clean nickel sample "flags" were fitted and the filament was decontaminated in the mass spectrometer[17]. A set of five filament beads was cleaned in this way and then loaded with samples; it was essential to avoid getting any of the sample on the tungsten filament for this caused fractionation and high apparent ^{7}Li/^{6}Li isotope ratios. Before each analysis the platinum lining of the ion box was removed and replaced by one which had been cleaned in boiling nitric acid.

When the isotope ratio of a standard sample was measured with this machine, the values found differed from those obtained with other mass spectrometers by 2–3%. Thus the National Bureau of Standards lithium carbonate sample, which yields a value of about 12.5 both with an M.S.5[18] and with an American machine[6], gave values ranging from 12.1 to 12.3. As this discrimination could not be eliminated, and was not constant over long periods of time, the N.B.S. sample was measured with each series of determinations and the value obtained used in a procedure to eliminate the effect of this variable discrimination.

METHOD

Preparation of the tracer solution

Weigh out about 10 mg of enriched lithium sulphate, dissolve in demineralised water, add a few drops of concentrated hydrochloric acid and make up to 1 l.

Weigh out about 250 mg of AnalaR barium nitrate, dissolve in demineralised water, add a little concentrated nitric acid and make up to 1 l.

Weigh out about 1 g of Johnson, Matthey's "Specpure" lithium carbonate in a platinum crucible and dissolve in dilute sulphuric acid. Expel the excess sulphuric acid and heat finally in a furnace at 700°C. From the lithium sulphate prepare 500 ml of a solution of accurately known lithium content. Take 5 ml of this solution, add a few drops of concentrated hydrochloric acid, and make up to 1 l with demineralised water. This solution is used for the calibration of the tracer.

Clean five platinum crucibles. Into four of them weigh out about 1 g of the standard solution and take to dryness under an infra-red lamp. Weigh out between 0.5 and 1.5 g of tracer solution into each platinum crucible, add 1 ml of barium nitrate solution and take to dryness. The quantities of the tracer and standard solutions should be chosen so that the ^{7}Li/^{6}Li isotope ratio lies in the range 0.7–1.3. Dissolve the residue in a small quantity of demineralised water and transfer to the nickel "flag" of a mass spectrometer source.

Treatment of samples

Weigh out 1–2 g of the tracer solution into each of five platinum crucibles and take to dryness under an infra-red lamp. Weigh out 200–300 mg of the sample into four of the crucibles. To each crucible add (1) 5 ml 40% hydrofluoric acid, (2) 5 ml 40% hydrofluoric acid and 5 ml 72% perchloric acid, (3) 5 ml 72% perchloric acid, and heat to dryness after each addition. Cover the crucible with a platinum lid and heat in a furnace at 500–520°C for 30 min. When cool, add 5 ml demineralised water, break up the residue with a glass rod, and heat until nearly boiling. Transfer the solution and washings to a 50 ml centrifuge tube, and clean the crucible with a paper tissue followed by concentrated nitric acid and demineralised water. After centrifuging return the aqueous extract to the crucible and take to dryness under an infra-red lamp. Heat to dryness first after the addition of 5 ml and then again after the addition of 2 ml of concentrated nitric acid. Add a few drops of demineralised water and transfer a portion of the solution to the nickel "flag" of a mass spectrometer source.

RESULTS AND DISCUSSION

Evaluation of results

All ratios have been expressed as the ^{7}Li/^{6}Li atomic ratio. The isotope ratio R_M, found for the mixture of X atoms of normal lithium and Y atoms of lithium 6 tracer, is given by the following relation:

$$R_M = \frac{X \cdot A_{7N} + Y \cdot A_{7T}}{X \cdot A_{6N} + Y \cdot A_{6T}}$$

where A_{7N} is the percentage abundance of ^{7}Li in normal lithium, *etc.*

$$X = Y \frac{R_M \cdot A_{6T} - A_{7T}}{A_{7N} - R_M \cdot A_{6N}}$$

If X and Y are replaced by x and y, the weights of normal and tracer lithium that have been mixed, then

$$x = y \frac{R_M \cdot A_{6T} - A_{7T}}{A_{7N} - R_M \cdot A_{6N}} \cdot \frac{\text{Atomic weight of normal lithium}}{\text{Atomic weight of tracer lithium}}$$

This can be expressed more conveniently in terms of isotope ratios:

$$x = y \frac{R_M - R_T}{R_N - R_M} \cdot \frac{7\,R_N + 6}{7\,R_T + 6} \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

where

R_N is the isotope ratio for normal lithium
R_T is the isotope ratio for lithium 6 tracer,
R_M is the isotope ratio for the mixture of a weight x of normal lithium with a weight y of lithium 6 tracer

If lithium 7 is used as a tracer, equation (1) becomes

$$x = y \frac{R_T - R_M}{R_M - R_N} \cdot \frac{7\,R_N + 6}{7\,R_T + 6} \quad \ldots\ldots\ldots\ldots\ldots \quad (2)$$

Equation (1) ignores the systematic errors that are introduced by a mass spectrometric measurement. If r and R are the true and measured isotope ratios, and D is the discrimination factor

$$r = D\,R$$

D may differ from unity by several percent and varies with focussing conditions and between different mass spectrometers.

The effect of discrimination can be almost completely eliminated if the concentration of the tracer solution is determined by isotope dilution with normal lithium. If the same quantity y of tracer is mixed with an accurately known quantity x' of normal lithium, and the isotope ratio found for the mixture is R'_M:

$$x' = y \frac{R'_M - R_T}{R'_N - R'_M} \cdot \frac{7\,R'_N + 6}{7\,R_T + 6} \quad \ldots\ldots\ldots\ldots\ldots \quad (3)$$

The quantity x of normal lithium in a sample is then effectively found from equation (4)

$$x = x' \frac{R'_N - R'_M}{R'_M - R_T} \cdot \frac{R_M - R_T}{R_N - R_M} \cdot \frac{R_N + 0.86}{R'_N + 0.86} \quad \ldots\ldots\ldots\ldots \quad (4)$$

In this equation discrimination is completely cancelled if R_N and R'_N, the isotope ratios of the normal lithium in the samples (G-1 or W-1) and in the standard ("Specpure" lithium), are the same. When they are not identical, the error is very small. Thus if R_N and R'_N differ by 10% and if the discrimination is 10%, the error in x is 0.05%.

Calibration of lithium 6 tracer

It is shown above that the effects of discrimination can be largely eliminated by measuring the concentration of the tracer solution by isotope dilution with normal lithium, but this assumes that the discrimination is constant. The mass spectrometer with which these measurements were made showed unusual discrimination for lithium, and the degree of discrimination was not constant over long periods of time. In order to eliminate the effect of this variation, an isotopic standard sample of lithium was measured with each series of determinations. The standard used was the N.B.S. lithium carbonate sample. If the true concentration of the tracer solution is c and the true ratio for the isotopic standard is r, then for a discrimination factor D, the values found will be approximately cD and r/D. Thus the product of the values found for the concentration of the tracer solution and the isotope ratio of the standard will be very nearly constant for small changes in D.

It was possible to introduce a further 1% discrimination by operating the ion source with the focus plates at a potential which was only 50 V less than the full, accelerating potential of 2000 V (Condition A), instead of at the more usual 200–250 V difference (Condition B). All measurements for the calibration of the lithium 6 tracer were made under these two conditions. The concentrations found are listed in Table I.

The values of the product $c'R'$ found under the two sets of focussing conditions are 21.275 and 21.286 respectively, that is the product is constant well within the limits of experimental error. For any one set of determinations of lithium in a sample, the relevant concentration of the lithium 6 tracer solution may be calculated from the value found for the ^{7}Li/^{6}Li ratio of the N.B.S. isotopic standard and the above product $c'R'$. For the determination of lithium in G-1 and W-1, the value found for the N.B.S. standard was 12.10, so a value of 1.759 μg/ml was used for the concentration of the tracer.

Calibration of lithium 7 tracer

The concentration of the lithium 7 tracer was determined immediately before

TABLE I

CALIBRATION OF THE LITHIUM 6 TRACER

Focussing conditions	*Concentrations found for tracer solution µg/ml*	*Mean value c'*	*Isotope ratio for N.B.S. standard R'*	*Product c'R'*	*Mean value and standard error*
Condition A	1.746 1.758 1.766 1.769	1.760	12.09	21.28	21.28 ± 0.08
Condition B	1.722 1.756 1.733 1.762	1.743	12.21	21.29	

Concentration of "Specpure" standard used for calibration: 3.6338 µg/ml.

(determination 1) and immediately after (determination 2) the measurements for G-1 and W-1. As the two results are not significantly different, they have been combined to give an average calibration.

TABLE II

CALIBRATION OF THE LITHIUM 7 TRACER

	Concentrations of "Specpure" standard µg/ml	*Concentrations found for tracer solution µg/ml*	*Mean value*	*Total mean value and standard error*
Determination 1	3.0139	5.31 5.40 5.41	5.37	$5.38_2 \pm 0.018$
Determination 2	0.9738	5.35 5.37 5.39 5.45	5.39	

Isotope ratio of lithium in G-1 and W-1

These results have been expressed as the ratio of the ^{7}Li/^{6}Li isotope ratio found for the lithium in the rock to the value found for the N.B.S. standard. (See Table III.)

The lithium contents of G-1 and W-1

In Table IV, the standard errors quoted have been calculated from the standard errors of the determination, of the calibration of the tracer solution, and of the

TABLE III

THE NATURAL ISOTOPE RATIO OF LITHIUM IN G-1 AND W-1

Sample	$\frac{R_N \text{ found for lithium in sample}}{R_N \text{ found for N.B.S. Standard}}$	*Mean value*
G-1	0.990 0.994 0.996	0.993
W-1	0.983 0.995 0.996 1.012	0.997

TABLE IV

LITHIUM CONTENTS OF G-1 AND W-1 BY STABLE ISOTOPE DILUTION ANALYSIS

Sample	*Determined by isotope dilution with lithium 6*			*Determined by isotope dilution with lithium 7*		
	Sample weight mg	*Lithium found p.p.m.*	*Mean value and twice total standard error*	*Sample weight mg*	*Lithium found p.p.m.*	*Mean value and twice total standard error*
	325.1	21.0		631.6	20.8	
G-1	176.2	21.4	21.6 ± 0.8	376.4	20.8	20.9 ± 0.6
	155.3	21.8		525.3	21.0	
	65.6	22.2		691.5	21.1	
	220.3	12.3		359.5	12.5	
W-1	89.9	12.6	12.6 ± 0.4	562.9	12.6	12.6 ± 0.4
	83.6	12.7		554.7	12.6	
	254.2	12.8		488.2	12.8	

determination of the normal lithium isotope ratio in the two samples and in the N.B.S. standard. The fact that there is no significant difference between the results obtained by the two methods suggests that they are independent of mass spectrometric discrimination and that there is no significant fractionation in the chemical treatment of the samples.

Table V records the results obtained for G-1 and W-1 by various methods. The accuracy of the flame photometer method is stated as 5 p.p.m.

Comparison of the methods of analysis by isotope dilution with lithium 6 and with lithium 7

A comparison of the formulae used to evaluate results shows that it is not necessary to measure the natural ^{7}Li/^{6}Li isotope ratio for a determination made by isotope dilution with lithium 6, although it is important for a determination with lithium 7. The expressions which include the normal lithium isotope ratio R_N and approximate values of R_M are:

Determination by lithium 6 $\dfrac{R_N + 0.86}{R_N - R_M}$ R_N 12.3, R_M 0.5–1.5

Determination by lithium 7 $\dfrac{R_N + 0.86}{R_M - R_N}$ R_N 12.3, R_M 40–100

TABLE V

LIHTIUM CONTENTS OF G-1 AND W-1 BY DIFFERENT METHODS

Analyst	*Method*	*Lithium p.p.m.*	
		G-1	*W-1*
Present Method	Stable isotope dilution	21.3	12.6
Ellestad, Horstman[12]	Flame photometry	24	14
Horstman[13]	Flame photometry	22	14
Jury[1]	Optical spectrography	21.7	15.9
		22.1	14.3
		24.5	16.0
Mitchell[19]	Optical spectrograhpy	19	9
Gorfinkle, Ahrens[19]	Optical spectrography	23	9
Nockolds[19]	Optical spectrography	25	20

In the case of lithium 6, the expression is very insensitive to changes in R_N, and assuming a value of 1.0 for R_M, a change of 1% in R_N alters the expression by 0.15%. For lithium 7 determinations, assuming a value of 100 for R_M, the same change in R_N changes the expression by 1.07%. Values reported for the isotope ratio of lithium in minerals and commercial chemicals lie in the range 12.3–12.9. Thus if it is assumed that the natural lithium isotope ratio in a sample is 12.6, for a determination by isotope dilution with lithium 6, the maximum error caused by this assumption would be 0.37%. The corresponding error for a determination with lithium 7 is 2.6%.

Lithium in Cornish china clay

The lithium 6 method was applied to two samples of Cornish china clay containing 0.1–0.3% of lithium. Because of the very high lithium content the spike was added to an aliquot of the perchloric acid extract instead of directly to the sample. An insoluble residue remaining after the hydrofluoric acid–perchloric acid treatment was examined by the Lawrence-Smith sintering method.

0.5–1 g of sample was attacked by hydrofluoric and perchloric acids in the usual way except that the final addition of perchloric acid was not taken to dryness; instead it was diluted and the solution and the residue were washed into a centrifuge tube. The solution was poured off into a standard flask, and the residue washed with hot water, hot nitric acid, and then twice with hot water. The washings were added to the solution in the flask and made up to volume. An aliquot of this solution was mixed with an aliquot of the tracer, taken to dryness and analysed in the usual way.

The washed residue was transferred to a platinum crucible, spiked with lithium 6 tracer, dried, and mixed with 1 g of Johnson, Matthey's "Specpure" calcium carbonate and 0.5 g of AnalaR ammonium chloride. The crucible was covered with a platinum lid, placed in a hole in an asbestos mat, and the lower half of the crucible heated over a Meker burner, gently at first and then to redness. When cool, 1 g of ammonium chloride was added and the process repeated. The contents of the crucible were treated with hot hydrochloric acid — a small quantity of a white material remained undissolved and was discarded. The solution was neutralised with ammonia and calcium was precipitated by ammonium carbonate; the supernatant liquid was taken to dryness, ammonium salts expelled by heating, and the residue treated twice with nitric acid, and analysed in the mass spectrometer. A blank determination for the lithium in the reagents was obtained by the same procedure; the value of 0.1 μg is 1–2% of the quantity of lithium found in the residues, or 0.01–0.02% of the total quantity of lithium found in the samples.

The results of this determination are recorded in Table VI; a value of 12.6 was assumed for the ^{7}Li/^{6}Li isotope ratio for the lithium in the clay. The spectrographic results included for comparison were obtained by HENDERSON, OWERS AND WEBB at Woolwich for the lithium removed by treatment with hydrofluoric and perchloric acids; spectrographic analysis of the residues showed no significant lithium content[20].

The value quoted for sample M6719 is supported by a second determination of 0.309%. This value would be expected to be slightly low, for it was obtained for the lithium in the perchloric acid extract only; the washings of the residue and the tube were lost when a breakage occurred in the centrifuge.

A combined chemical procedure of an acid treatment followed by a fusion similar to that used for these samples was recommended by KALLMANN[21], but these results,

TABLE VI

LITHIUM CONTENTS OF TWO CLAY SAMPLES

Sample	*Sample weight g*	*% Lithium found by HF/HClO$_4$ treatment*	*Residue weight g*	*% Lithium found in residue by L-S sinter*	*Total % lithium in sample*	*Mean value*	*Spectrographic value*
MD/E680/A3 M6701 ore 71	0.4880	0.138	0.0499	0.0011	0.139	0.138	0.14
	0.7531	0.137	0.0806	0.0007	0.138		
MD/E698/A3-170 M6719 ore 71	0.9635	0.316	0.2184	0.0015	0.318	0.318	0.32–0.33
Value found for ^{7}Li/^{6}Li isotope ratio of N.B.S. standard							12.30
Value used for concentration of lithium 6 tracer solution							1.730 μg/ml

although only on one type of material, support the contention of SYKES[14] that treatment with hydrofluoric acid is adequate for the determination of lithium in its ores.

CONCLUSIONS

The method of isotope dilution has been applied to the determination of lithium in two standard rocks. The values obtained are G-1 21.3 p.p.m. and W-1 12.6 p.p.m. After making allowance for possible errors in the calibration of the tracer solutions and the determination of the natural lithium abundance ratios, it seems likely that these values are correct to within at least ± 5%. Good agreement is shown by the results obtained by isotope dilution analysis and spectrographic analysis for china clay containing 0.1–0.3% lithium.

The precision of the method is better than that attained by any other current analytical method; the coefficient of variation for four results is usually ± 1–2%. By using both lithium 6 and lithium 7 as tracers it has been established that no significant errors arise from isotopic fractionation or mass spectrometric discrimination. If the ^{7}Li/^{6}Li isotope ratio of lithium in a rock sample is assumed to be 12.6, for a determination by isotope dilution with lithium 6, the error introduced by this assumption is not likely to be greater than 0.5%.

The method has been used for the determination of lithium contents of samples in the range 1 μg to 3 mg; a quantity as small as $3 \cdot 10^{-10}$ g, has been measured in a blank determination, but even this does not represent the ultimate sensitivity of the method.

SUMMARY

A method is described for the determination of lithium in rocks by the method of stable isotope dilution. 50 mg to 500 mg of the sample are used for each determination. The sample is mixed with a known quantity of enriched lithium and is then decomposed by a mixture of hydrofluoric and perchloric acids. The separation of the alkali metals from iron and aluminium is based on the thermal decomposition of the perchlorates. For mass spectrometric measurements it is not necessary to separate the lithium from the other alkali metals.

The values obtained for the lithium contents of two standard rocks are: G-1, 21.3 p.p.m.; W-1, 12.6 p.p.m. Independent determinations, made using both lithium 6 and lithium 7 as tracers, have established that no significant systematic errors are caused by isotopic fractionation.

Results obtained for two clay samples containing 0.1–0.3% of lithium show good agreement with spectrographic values.

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COULOMETRIC TITRATIONS WITH MERCURY(I) AND (II)

DETERMINATIONS OF SECONDARY AMINES AND MERCAPTANS

by

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Because recent studies[1] have shown that electrolytically generated mercury (I and II) reagents are very sensitive titrants for certain precipitation titrations in aqueous media, their application to the titration of organic functional groups in nonaqueous solutions was investigated. One of the limitations of volumetric procedures in nonaqueous media is the necessity of adding anhydrous titrant to the solution. In many cases this is required because of the low solubility of water in the media, or because traces of water will interfere with the desired reaction. For example, a titration in which silver nitrate is used as a titrant must be carried out in an alcohol–water mixture to keep the silver nitrate soluble. The coulometric technique provides a means of adding reagent to a solution without introducing solvent. The chief limitation in selecting the solvent is that it be polar enough to dissolve a small amount of electrolyte to aid the passage of current used to generate the reagent. Thus it seemed desirable to investigate nonaqueous systems in order to emphasize the advantage of coulometric titrations of organic functional groups involving precipitation. The systems chosen for investigation were the titration of amines and mercaptans with mercury(II).

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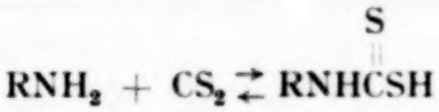
AMINES

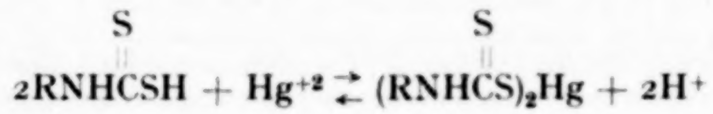
When primary or secondary aliphatic amines are reacted with carbon disulfide the corresponding dithiocarbamic acid is formed. This has been reported as the basis for estimating amines by CRITCHFIELD AND JOHNSON[2] who used alkali to titrate the dithiocarbamic acid formed in this reaction. The titration is one of a weak acid, hence the method lacks sensitivity for low concentrations of amines. On the other hand, heavy metal dithiocarbamates have been reported to have a very low solubility, and hence it should be possible to titrate very small amounts of dithiocarbamic acid with electrolytically generated mercury(II). Because the reaction of primary and secondary amines with carbon disulfide appeared to be quantitative, it was hoped that the use of electrolytically generated mercury(II) reagents would provide a more sensitive titrimetric procedure for amines.

The general reaction between carbon disulfide and aliphatic amines can be written as,



$$RNH_2 + CS_2 \rightleftarrows RNH\overset{\overset{S}{\|}}{C}SH \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

The resulting dithiocarbamic acids are weak acids with pK values of about 6 in water[3]. The reaction of the dithiocarbamic acid with mercury(II) ion proceeds as follows:



$$2RNH\overset{\overset{S}{\|}}{C}SH + Hg^{+2} \rightleftarrows (RNH\overset{\overset{S}{\|}}{C}S)_2Hg + 2H^+ \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

Very little information is available in the literature concerning the mercury derivatives, though they are reported[4] to be insoluble in water and some organic solvents. Recently, BOBTELSKY[4] titrated small amounts of mercury(II) heterometrically using the sodium salt of diethyldithiocarbamic acid. Other workers[5] have also reported the determination of mercury using dithiocarbamates.

Reagents and apparatus

All amines used in this study were Eastman Kodak White Label chemicals. The aliphatic amines were purified by distillation.

The organic solvents used were of various grades of purity. Acetone and methanol were of analytical reagent grade (Mallinckrodt). Carbon disulfide was "pure" grade (Merck) as were other organic solvents used in this work. The isopropanol was further purified by distilling from silver nitrate crystals to remove chloride impurity.

When required, anhydrous sodium perchlorate was obtained by drying Fisher sodium perchlorate monohydrate at 110°C overnight.

The apparatus used in these studies is described in an earlier publication[1]. Mercury-coated gold electrodes were used as generator and indicator electrodes.

Exploratory titrations in various solvents

To ascertain the effects of different solvents, the titration of diethylamine was carried out in the presence of a 5% (by volume) solution of carbon disulfide and 0.5 F sodium perchlorate in the following solvents: acetonitrile, dimethylformamide, methanol, isopropanol, *tert*-butanol, acetone and methylcellosolve. Fig. 1 shows the potentiometric titration curves obtained in these solvents. Acetone and methanol appeared to give titration curves which were the most suitable for quantitative purposes and hence were examined in detail.

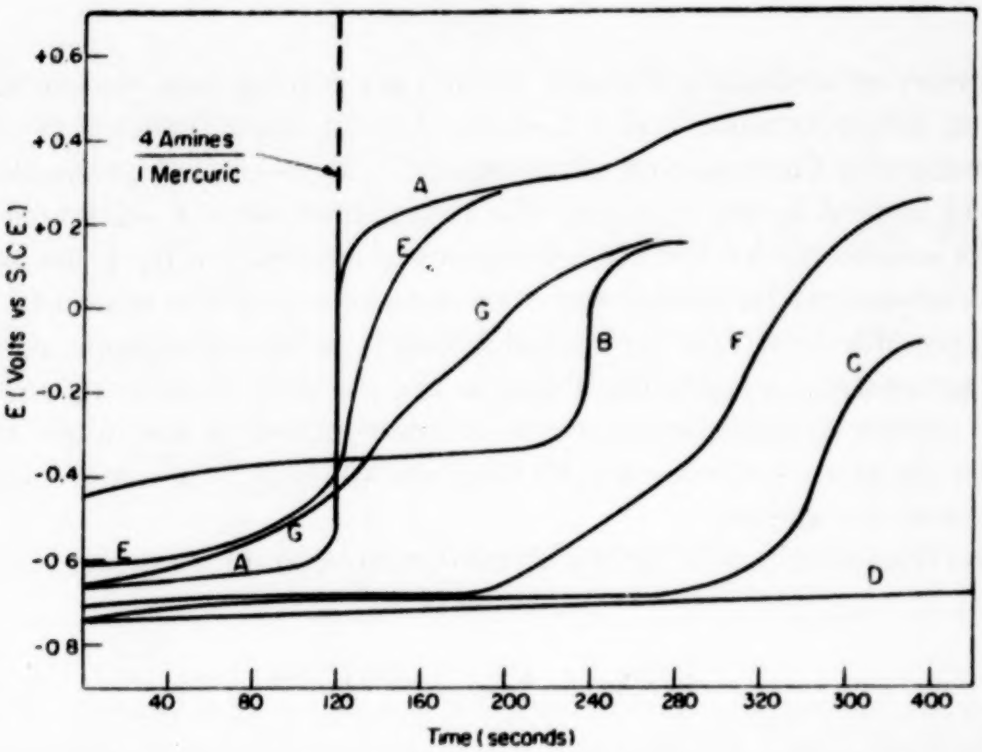


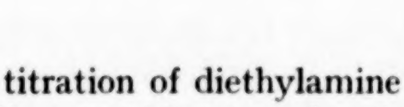
Fig. 1. Titration curves of $2.43 \cdot 10^{-5}$ equivalents of diethylamine in 100 ml of the following solvents: A. 5% carbon disulfide–95% acetone. B. 5% carbon disulfide–95% methanol. C. 5% carbon disulfide–95% isopropanol. D. 5% carbon disulfide–95% *tert*-butanol. E. 5% carbon disulfide–95% methylcellosolve. F. 5% carbon disulfide–95% dimethylformamide. G. 5% carbon disulfide–95% acetonitrile. The supporting electrolyte was 0.5 *F* sodium perchlorate, and the generating current was 20.00 mA. These curves were recorded automatically using a Weston recording potentiometer.

Titrations in methanol

A study was made of the titration of diethylamine in methanol–carbon disulfide mixtures containing 0.5 *F* sodium perchlorate and carbon disulfide from 0.01% to 5% by volume. As the percentage of carbon disulfide was increased, it was obvious that some reaction other than the direct reaction between mercury and the amine became predominant. Potentiometrically, this second reaction was far more sensitive than the direct reaction of mercury(II) with the amine. Solvent systems containing more than 5% carbon disulfide by volume did not improve the general shape of the curve.

Fig. 2, which shows the titration curves of *sec*-butylamine and triethylamine in a 5% solution of carbon disulfide in methanol, indicates that the mechanism proposed in equation (1) did not represent the titration of the tertiary amine because only primary and secondary amines should form dithiocarbamic acids. Since all three types of amines seemed to give identical titration curves with a stoichiometry of two amines per mercury ion, it was evident that the reaction of carbon disulfide with amine did not result in a dithiocarbamic acid.

Carbon disulfide is known to react with alcohols to form xanthates, the velocity depending upon the alcohol[6].



$$\mathrm{ROH} + \mathrm{CS_2} \rightleftarrows \mathrm{RO}\overset{\overset{\displaystyle \mathrm{S}}{\|}}{\mathrm{C}}\mathrm{SH} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

With low molecular weight alcohols, the reaction is slow in neutral or acid media. In alkaline solution, however, carbon disulfide can react stoichiometrically with an alcohol due to neutralization of the xanthic acid. The amine then reacts quantitatively

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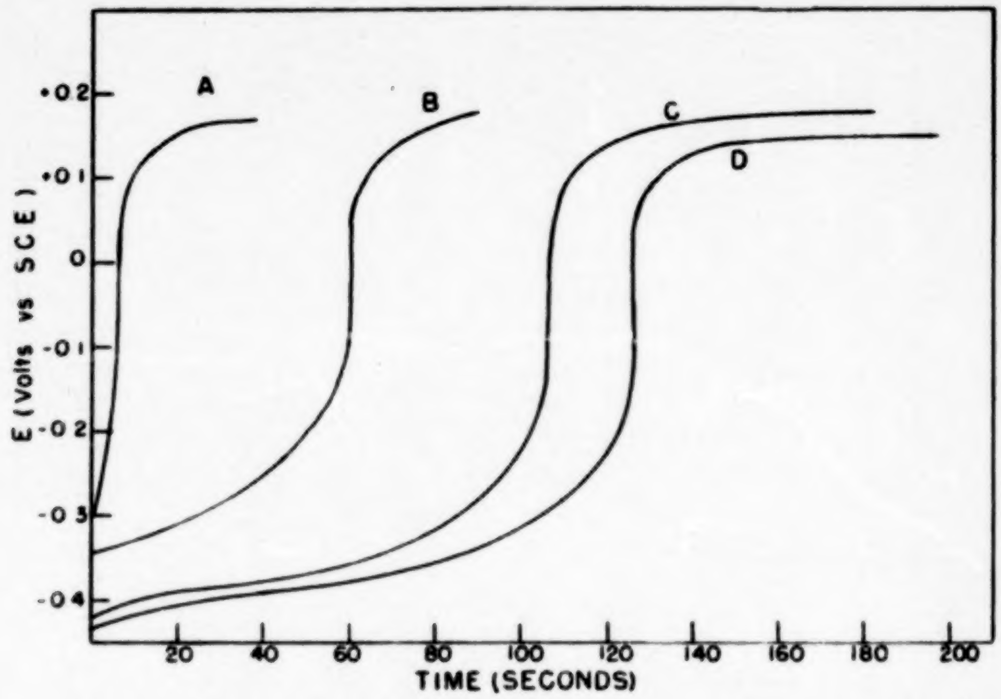
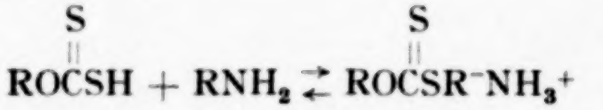
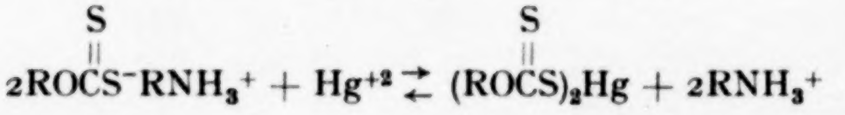


Fig. 2. Automatic potentiometric titrations in 100 ml of 5% carbon disulfide–95% methanol solution. A. Blank titration. B. $1.25 \cdot 10^{-5}$ equivalents of sodium hydroxide. C. $1.80 \cdot 10^{-5}$ equivalents of triethylamine. D. $2.47 \cdot 10^{-5}$ equivalents of *sec*-butylamine. The supporting electrolyte was 0.5 *F* sodium perchlorate, and the generating current was 20.00 mA.

with the xanthic acid to form a salt which is then titrated with mercury according to the following reactions:



$$\mathrm{RO\overset{\overset{S}{\|}}{C}SH + RNH_2 \rightleftarrows RO\overset{\overset{S}{\|}}{C}SR^{-}NH_3^{+}} \quad \ldots\ldots\ldots\ldots \quad (4)$$

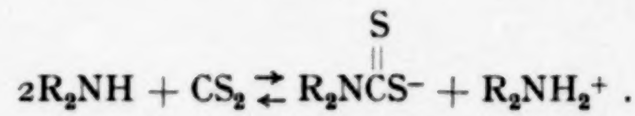


$$\mathrm{2RO\overset{\overset{S}{\|}}{C}S^{-}RNH_3^{+} + Hg^{+2} \rightleftarrows (RO\overset{\overset{S}{\|}}{C}S)_2Hg + 2RNH_3^{+}} \quad \ldots\ldots \quad (5)$$

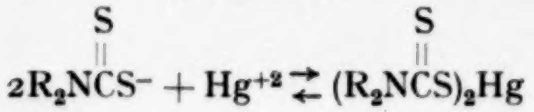
Proof for this mechanism is given in Fig. 2 where the titration curve of 10^{-4} *F* sodium hydroxide in this medium is shown to give a titration curve similar to that obtained with an amine. This indicates that the titrated substance was not a product of the reaction of amine with carbon disulfide, but more likely a xanthate. Furthermore, when carbon disulfide was allowed to be in contact with methanol for a longer period of time, the blank was found to increase slowly at a rate of about 10^{-6} equivalents per minute. It was evident, then, that the use of methanol as a medium for this titration was not advisable for quantitative purposes.

Titrations in acetone

In acetone medium, the titration has a stoichiometry of four amines per mercury ion (Fig. 1). This corresponds to the following set of reactions.



$$\mathrm{2R_2NH + CS_2 \rightleftarrows R_2N\overset{\overset{S}{\|}}{C}S^{-} + R_2NH_2^{+}} \quad \ldots\ldots\ldots\ldots \quad (6)$$



$$\mathrm{2R_2N\overset{\overset{S}{\|}}{C}S^{-} + Hg^{+2} \rightleftarrows (R_2N\overset{\overset{S}{\|}}{C}S)_2Hg} \quad \ldots\ldots\ldots\ldots \quad (7)$$

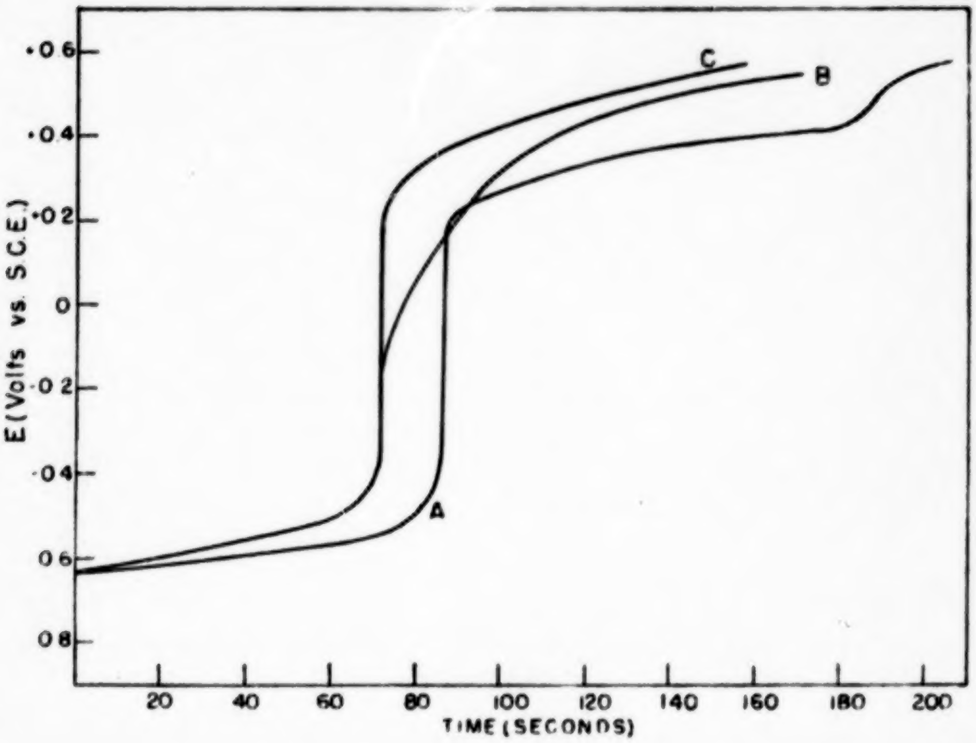


Fig. 3. Titrations of sodium and diethylammonium salts of diethyldithiocarbamic acid at a generating current of 20.00 mA. A. Diethylammonium diethyldithiocarbamate in 100 ml of 100% acetone containing 0.5 *F* sodium perchlorate. B. Sodium diethyldithiocarbamate in 100 ml of 100% acetone containing 0.5 *F* sodium perchlorate. C. Sodium diethyldithiocarbamate in 100 ml of 75% acetone–25% carbon disulfide containing 0.5 *F* sodium perchlorate. These curves were recorded automatically using continuous generation of reagent.

The validity of the above mechanism was established by reacting diethylamine with excess carbon disulfide in acetone solution and then isolating the product in reaction 6. When the excess acetone and carbon disulfide were distilled off under vacuum, a yellowish-white solid remained. Elemental analysis of this substance agreed with the formula $C_9H_{22}N_2S_2$ in equation 6.

% Element	C	N	H	S
Found	48.97	12.79	9.70	29.08
Calc.	48.62	12.61	9.97	28.80

A sample of this compound was also titrated coulometrically in 100% acetone as shown in Fig. 3. The first large jump in potential is due to the completion of reaction 7; the second smaller jump is presumably due to a reaction of the diethylammonium ion with mercury ion:

$$Hg^{+2} + x\, R_2NH_3^{+} \rightleftarrows Hg(R_2NH)_x^{+2} + x\, H^{+} \quad \ldots\ldots\ldots \quad (8)$$

Since a titration of the sodium salt of diethyldithiocarbamic acid did not show a definite second break (Fig. 3), it was concluded that the second potential jump in Fig. 3 was due to the reaction shown in equation (8). In addition, the titration curve of the sodium salt of diethyldithiocarbamic acid in 100% acetone (Fig. 3) showed considerable curvature past the end-point, which was attributed to slight dissociation of the dithiocarbamic acid to carbon disulfide and to the free amine. The presence of 25%

carbon disulfide by volume improved the sharpness of the end-point break, thereby emphasizing the need for a large excess of carbon disulfide in carrying out this titration. Amounts of water up to 10% were found to cause no significant interference in these titrations.

Procedure. The following procedure was used to titrate the secondary amines listed in Table I. A solvent mixture of 25 ml carbon disulfide and 75 ml acetone was made 0.5 *F* in sodium perchlorate by dissolving 7.1 g of the monohydrate. This solution was deaerated in the titration cell using nitrogen for 10 min. Mercury(II) was then generated until the potential of the mercury electrode was —0.200 V *versus* S.C.E., a potential on the steepest part of the titration curve. The blank (perhaps ammonia) corresponded to about 5 sec of generation at 20.00 mA. The amine sample was then added and the solution titrated back to —0.200 V.

With the exception of di-*n*-butylamine, a 0.0050 ml sample of each of the amines in Table I was titrated at a generating current of 20.00 mA. Standard solutions of di-*n*-butylamine in acetone were made up by weight, and 1.000 ml aliquots of these solutions were taken for analysis.

As Table I shows, the following secondary amines were successfully titrated in this medium: diethylamine, di-*n*-propylamine, di-*n*-butylamine, morpholine and cyclohexylamine.

TABLE I

TITRATIONS OF SECONDARY ALIPHATIC AMINES IN 100 ml OF 25% CARBON DISULFIDE–75% ACETONE SOLVENT

All solutions were titrated to —0.200 V *versus* S.C.E.

Amine	*Amount taken mg*	*Current mA*	*Amount found, mg*	*% Error*
Diethylamine	3.56	20.00	3.53	—0.84
	3.56	20.00	3.55	—0.28
Di-*n*-propylamine	3.70	20.00	3.71	—0.27
	3.70	20.00	3.67	—0.81
Morpholine	5.01	20.00	5.05	—0.80
	5.01	20.00	5.01	0.00
Cyclohexylamine	4.33	20.00	4.32	—0.23
	4.33	20.00	4.30	—0.70
Di-*n*-butylamine	7.680	20.00	7.671	—0.12
	7.680	20.00	7.679	—0.01
	7.680	20.00	7.670	—0.13
	3.840	10.00	3.840	0.00
	3.840	10.00	3.835	—0.13
	3.840	10.00	3.835	—0.13
	0.384	1.084	0.381	—0.78
	0.384	1.084	0.378	—1.56
	0.384	1.084	0.379	—1.30

Discussion

Tertiary amines cannot undergo reaction 6, and hence can be differentiated in this solvent system. Titrations of triethylamine in this solvent showed that only a reaction of the type given in equation (8) was taking place (Fig. 4). On the other hand, primary amines undergo reaction with carbon disulfide in the same manner as secondary

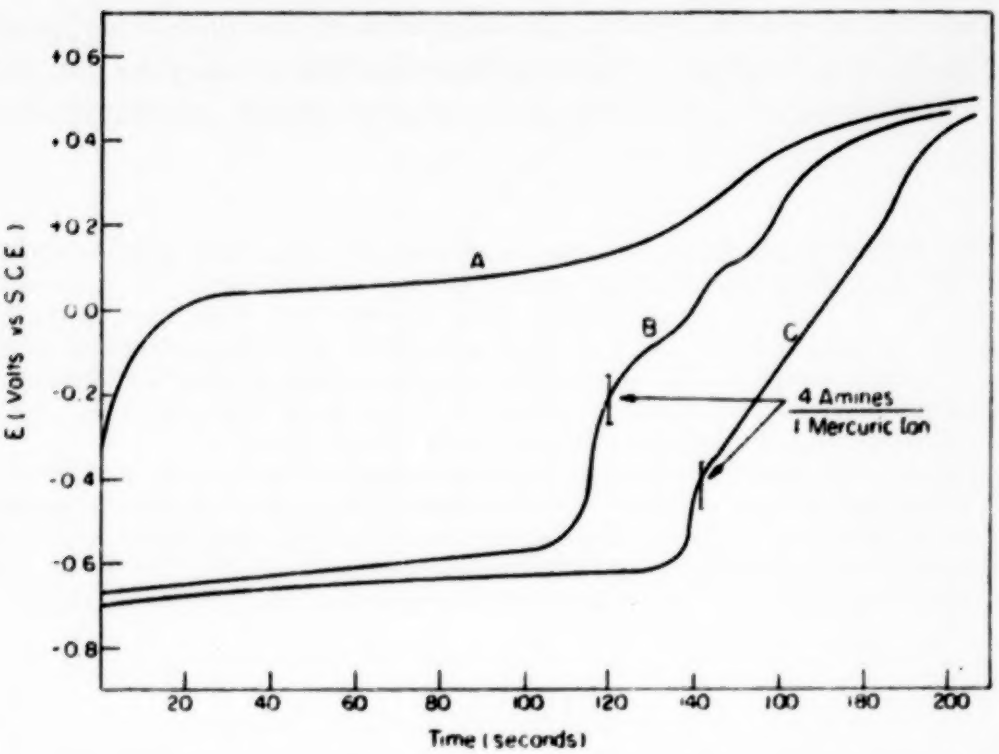


Fig. 4. Titrations of primary and tertiary amines in 100 ml of 75% acetone–25% carbon disulfide at a generating current of 20.00 mA. A. $1.80 \cdot 10^{-5}$ equivalents of triethylamine. B. $2.53 \cdot 10^{-5}$ equivalents of *n*-butylamine. C. $3.03 \cdot 10^{-5}$ equivalents of *n*-propylamine. Solutions contained 0.5 *F* sodium perchlorate anhydrous as a supporting electrolyte. These curves were recorded automatically using continuous generation of reagent.

amines. However, there is evidence in the literature which indicates that the reaction of a primary amine with acetone sets up a competitive equilibrium.

$$(CH_3)_2C=O + RNH_2 \rightleftarrows (CH_3)_2C=NR + H_2O \quad \ldots\ldots\ldots \quad (9)$$

If the above reaction occurs to a significant extent, the titration of the dithiocarbamate will give low results. Fig. 4 shows the titration curves of *n*-butylamine and *n*-propylamine in the acetone–carbon disulfide medium. The first potential break came 2–5% low for the titration of the dithiocarbamate ion. Two additional potential breaks appeared when the solution was 150 to 175% titrated, and were found not to be exactly reproducible from one titration to the next. This indicated that equilibrium conditions were not being reached during the course of this titration, a conclusion which was substantiated by comparing an automatically recorded titration curve for *tert*-butylamine with one recorded manually (Fig. 5). The manual titration curve had only one drawn-out potential break, which can be explained on the basis of a slow competitive equilibrium suggested above. For comparison, a manual titration curve of diethylamine is also shown in Fig. 5. Its curve has a sharp break, so presumably there was no competing equilibrium.

Excess perchloric acid (10^{-2} *F*) interfered with the determination by preventing the formation of the dithiocarbamate. The titration curve obtained in this acid solution had no break.

Excess sodium hydroxide (10^{-3} *F*) interfered with this determination only if it had been in contact with the deaerated carbon disulfide solution for 10 min or more. This

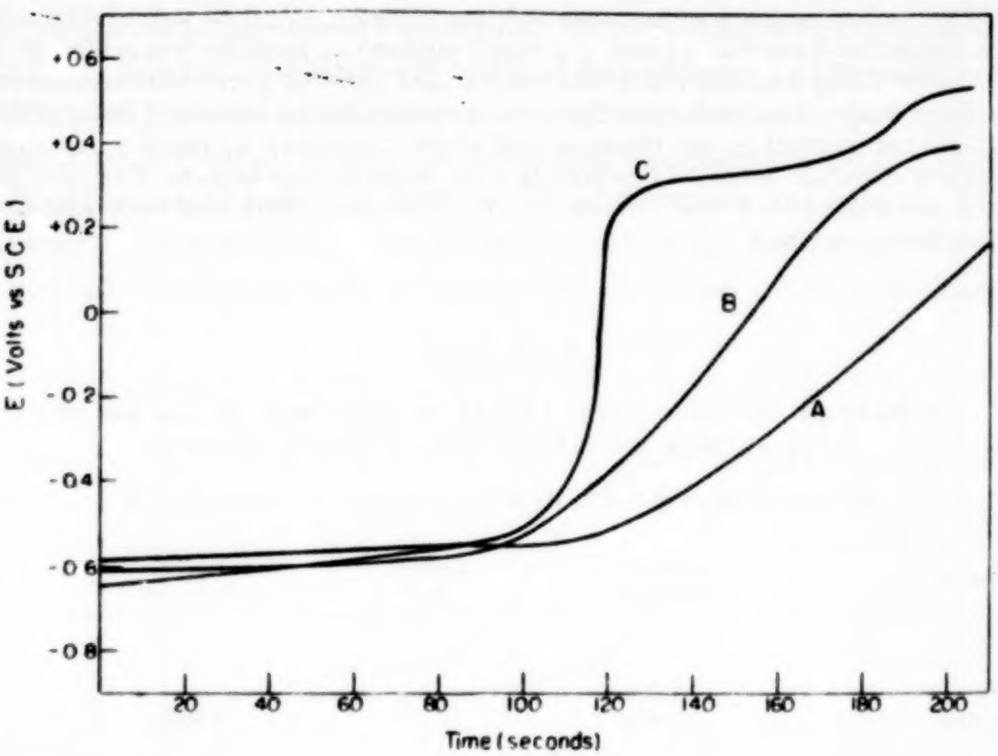


Fig. 5. Comparison of manual and automatic coulometric titrations for primary and secondary amines in 75% acetone–25% carbon disulfide solutions. A. Manual titration of $2.38 \cdot 10^{-5}$ equivalents of *tert*-butylamine. B. Automatic titration of $2.38 \cdot 10^{-5}$ equivalents of *tert*-butylamine. C. Manual titration of $2.43 \cdot 10^{-5}$ equivalents of diethylamine. Solutions contained 0.5 *F* sodium perchlorate anhydrous as a supporting electrolyte. A generating current of 20.00 mA was used.

interference was presumably caused by the hydrolysis of carbon disulfide[7]. Ammonia interfered with the titration even in small amounts (10^{-5} *F*) presumably as the result of a reaction of ammonia with carbon disulfide to form products which were reactive toward mercury(II).

The mercury titration of dithiocarbamates was briefly compared with one in which silver ion was generated. It was found that silver did not give a good titration curve with either primary or secondary amines in methanol, methylcellosolve or acetone when each solvent contained 25% carbon disulfide by volume. It appeared from the titration curves that the reaction was incomplete — similar to the effect noted in the titration of primary amines with mercury. It was thus concluded that silver would not be a feasible reagent for this titration.

Determination of secondary amines in the presence of primary amines

Because primary amines react incompletely with carbon disulfide, they constitute an interference in the determination of secondary amines in mixtures by the above procedure. This interference can be removed by reacting the primary amine with salicylaldehyde, forming a Schiff Base[8].

$$RNH_2 + HOC_6H_4CHO \rightleftarrows HOC_6H_4CHNR + H_2O \quad . \; . \; . \; . \; . \; . \; . \; . \quad (10)$$

The Schiff Base does not react with carbon disulfide or mercury ion, thus eliminating the interference of primary amines.

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Procedure. The amine mixture to be analyzed was added to 5 ml of salicylaldehyde in a 25-ml beaker. If the amine mixture was aqueous, a small amount of acetone was added to give a single liquid phase. The resulting solution was heated on a steam bath for 5 min to accelerate the formation of the Schiff Base which was indicated by the formation of an intense yellow coloration. This solution was then transferred to the titration cell which contained 95 ml of a deaerated 75% acetone – 25% carbon disulfide solution containing 0.5 *F* sodium perchlorate. This solution had been pretitrated to a potential of —0.200 V *versus* S.C.E. After the sample had been added, the solution was titrated back to —0.200 V.

TABLE II

TITRATIONS OF SECONDARY AMINES IN MIXTURES IN 100 ml OF 25% CARBON DISULFIDE–75% ACETONE SOLVENT

All solutions were titrated to —0.200 V *versus* S.C.E.

Amine	*Amount taken, mg*	*Current mA*	*Amount found, mg*	*% Error*
Triethylamine Di-*n*-butylamine	3.65 7.680	20.00	7.668	—0.15
Triethylamine Di-*n*-butylamine	14.58 7.680	20.00	7.682	+0.03
n-Butylamine Di-*n*-butylamine	3.70 7.680	20.00	7.674	—0.08
n-Butylamine Di-*n*-butylamine	14.80 7.680	20.00	7.679	—0.01
n-Butylamine Di-*n*-butylamine	37.0 7.680	20.00	7.686	+0.08
n-Butylamine Triethylamine Di-*n*-butylamine	3.70 3.65 7.680	20.00	7.685	+0.07

Results

The data in Table II indicate that the above procedure removed the interference of primary amines quantitatively. Tertiary amines also did not interfere at the concentrations studied.

Methanol interfered in this determination, presumably due to xanthate formation. Although 1% methanol did not cause a significant error, the titration of di-*n*-butylamine in 10% methanol produced a 15% positive error.

Titrations in the absence of carbon disulfide

In solutions containing water, aliphatic amines hydrolyze to produce hydroxyl ion which reacts with mercury(II).

Fig. 6 shows the titration curves of *sec*-butylamine and *tri*-ethylamine in aqueous 0.5M sodium perchlorate. A yellow precipitate was present at the conclusion of both titrations. The stoichiometry indicated a 2:1 ratio of amine to mercury. When this same titration was carried out in a 0.5M ammonium acetate buffer, the titration curve had no break. These facts indicate that the direct titration of aliphatic amines in the presence of water proceeds according to equation 8. This confirmed the assumption that there was no significant gain in sensitivity over the usual acid-base titration.

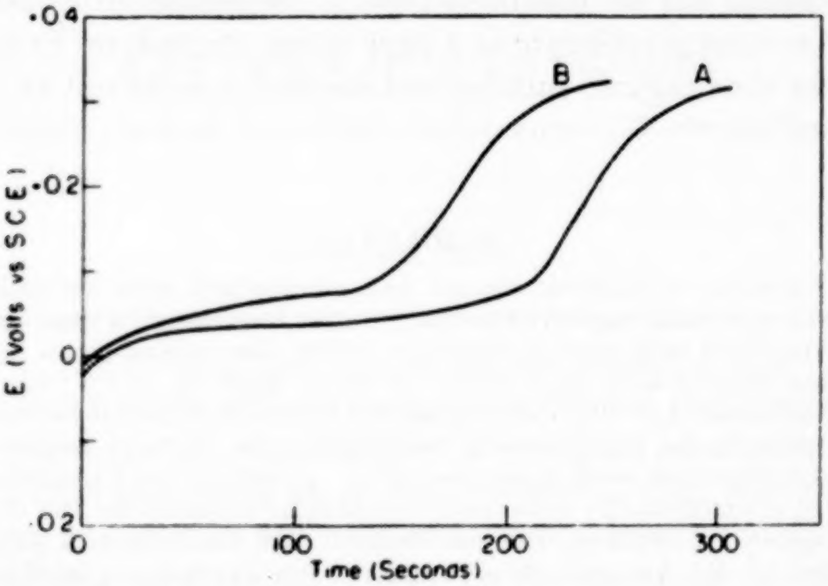

Fig. 6. Coulometric titration of amines in aqueous 0.5M sodium perchlorate. A. $2.47 \cdot 10^{-5}$ equivalents of *sec*-butylamine. B. $1.80 \cdot 10^{-5}$ equivalents of triethylamine. The generating current used was 20.00 mA.

MERCAPTANS

STRICKS, KOLTHOFF AND TANAKA[9] have reported the amperometric titration of mercaptans and disulfides using mercury(II) as a titrant. Their studies showed that only the sulfhydryl group reacted with mercury(II); disulfides had to be reduced with sodium sulfite prior to titration. A brief coulometric study of the titrations of several sulfur compounds confirmed their conclusions. It seemed worthwhile, however, to make a brief study to demonstrate the feasibility of coulometrically generating mercury(II) to determine sulfhydryl compounds.

Cysteine and mercaptoacetic acid gave well-defined titration curves in borate buffer at pH = 9.2. The representative results for cysteine shown in Table III indicate the

TABLE III

TITRATIONS OF CYSTEINE IN ABOUT 100 ml OF 0.5M SODIUM TETRABORATE AT pH 9.2

Titrations carried out to —0.200 V *versus* S.C.E.

Amount taken, mg	*Current mA*	*Number of trials*	*Amount found, mg*	*Std. dev. mg*	*Av. error %*
10.28	20.00	3	10.27	0.01	—0.10
5.141	20.00	3	5.137	0.008	—0.07
5.141	10.00	3	5.134	0.001	—0.14
1.285	5.00	3	1.279	0.003	—0.47
0.257	1.078	3	0.250	0.002	—2.72

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method to be comparable in accuracy to the amperometric method reported by KOLTHOFF *et al.*[10], in which they determined 7 to 50 mg of sulfhydryl sulfur with an accuracy of 2%. The results shown in Table III are accurate to within 2.7% for 0.3 mg of sulfhydryl sulfur. At higher concentrations, it can be seen that the accuracy is improved. Because the mercurimetric titration of sulfhydryl groups had been studied extensively by others[9,10], further work on the coulometric titration of this functional group did not seem justified.

Cysteine (disulfide) and di-*n*-butyl sulfide (organic sulfide) gave no breaks when titrations were carried out in unbuffered 60% methanol-40% benzene solutions containing $0.5M$ sodium perchlorate as a supporting electrolyte. From the above evidence, it was clear that organic sulfides and disulfides could not be titrated directly with mercury (I or II).

SUMMARY

A study of the titration of aliphatic amines and mercaptans with electrolytically generated mercury(II) reagent is reported. Amines were titrated after conversion to their corresponding dithiocarbamic acids by reaction with carbon disulfide. Using this procedure, a $3 \cdot 10^{-4}$ F solution of secondary amine was titrated with an accuracy of better than 1% and a concentration of $3 \cdot 10^{-5}$ F with an accuracy of better than 2%. Primary amines constituted an interference in this procedure but were removed prior to the titration with salicylaldehyde. Tertiary amines were found not to interfere. Comparable titrations with generated silver ion did not give quantitative results.

The application of electrolytically generated mercury(II) reagents for the titration of another organic functional group, sulfhydryl, was also studied. The titration of a sulfhydryl compound (cysteine) was studied briefly. Amounts of cysteine down to 1.29 mg in 100 ml of solution ($1.3 \cdot 10^{-4}$ F) were determined with an accuracy of better than 1%. Smaller amounts of cysteine down to 0.26 mg ($2 \cdot 10^{-5}$ F) were determined with about 3% accuracy.

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THE POLAROGRAPHIC DETERMINATION OF INDIUM IN ZINC-BASE ALLOYS

II. THE DETERMINATION OF INDIUM IN ZINC AND IN ZINC ALLOYS OF LOW ALUMINIUM CONTENT

by

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INTRODUCTION

In Part I of this series of papers[1], the nature of the problem was outlined and the literature relating to the polarography of indium was briefly reviewed. In particular, it was emphasised that a major difficulty arose from the fact that polarographic waves of cadmium and indium are almost coincident in nearly all commonly employed base electrolytes. The former element is likely to be present in most zinc alloys in concentrations significantly higher than the level of detection desired for indium (1 p.p.m.).

The development of a rapid method, based on the use of the derivative circuit of the linear sweep cathode ray polarograph[2,3] has been described. This method was shown to be satisfactory and sufficiently sensitive even in the case of complex alloys of the mazak type provided that the cadmium : indium ratio did not exceed 10:1. It was, however, considered that the present limited availability of cathode ray instruments necessitated the development of further methods which, although involving more complicated chemical separation, would require only conventional polarography.

A study of the literature listed in Part I[1] indicated three promising lines of approach. These were the separation of indium by means of 8-hydroxyquinoline in chloroform, employed by MILNER[4], the zinc oxide "collection" procedure of SEMERANO[5] and the use of an iodide base electrolyte to complex the cadmium and move its half-wave potential to a more negative potential than that of the uncomplexed indium. The work carried out to investigate the applicability of the first two of these techniques is described and discussed below.

EXPERIMENTAL AND DISCUSSION

AnalaR zinc oxide was used as the source of zinc for these experiments and "specpure" indium oxide was used as the source of indium. A mazak alloy of approximately the composition previously given[1] was used for trials of proposed methods.

All polarography was carried out at 25°C and *versus* the mercury pool anode. Three types of polarographs were employed to ensure that resolution of steps produced by any of the methods developed would be possible on any type of instrument likely to be used. The instruments employed were the Cambridge photographic-recording and pen-recording polarographs and a special research polarograph[6]. All potentials are quoted on the European sign convention. On this convention the saturated calomel electrode (S.C.E.) has been taken as + 0.246 V *versus* the normal hydrogen electrode (N.H.E.)

General

In order to check the efficiency of separations easily and quickly it was decided to employ radio-chemical techniques. A supply of a radioactive indium metal (^{114}In) was therefore obtained. The half life of this isotope was 49 days and disintegrated with emission of β-particles. The activity was such that 10 μg of indium in a total volume of 20 ml gave about 500 c.p.m. in a halogen-quenched liquid counter tube.

The use of 8-hydroxyquinoline

The use of a solution of 8-hydroxyquinoline in chloroform to extract the indium from a solution of pH 3.5, as employed by MILNER[4], was tried. It is reported in the literature[7] that cadmium forms an oxinate only above pH 4.6.

10-ml aliquots of a solution of zinc chloride, which contained 1 g zinc per 10 ml, were placed in 50-ml centrifuge tubes and 0.05-ml aliquots of radio-active indium solution (equivalent to 10 μg indium) were added. The pH values were then adjusted using a pH meter, the solutions were diluted to 20 ml and 1.5 ml aliquots of 0.5% 8-hydroxyquinoline in chloroform were added. The solutions were stirred vigorously for 5 min and centrifuged to separate the layers. The chloroform was then drawn off by means of a transfer pipette. After repeating the extraction three times with fresh portions of oxine solution, the solutions were poured into liquid counter tubes and counted. The standard count was obtained by counting a solution prepared as above but with the extraction procedure omitted.

Initial experiments showed that about 90% of the indium remained unextracted and that the extraction was causing a considerable lowering of the pH. Correction for this improved the figures but at various pH values over the range 2.58 to 4.55 the highest extraction was only 28.3%. These low recoveries were attributed to a competition for the 8-hydroxyquinoline between the indium and zinc and the concentration of the 8-hydroxyquinoline solution was therefore increased to 5%. This improved the recoveries to 65 to 58% over approximately the same pH range as previously employed, but even increasing the number of extractions failed to give further improvement. The procedure was therefore abandoned as useless in the presence of such a relatively high concentration of zinc.

The use of a "collection" procedure

The method of SEMERANO[5] in which the indium is "collected" on zinc oxide was next investigated. A 20-ml aliquot of zinc chloride solution containing radio-active indium and having a pH about 2.0 was prepared as above and was then shaken with zinc oxide for one h. After separation by centrifuging, the zinc oxide was dissolved in hydrochloric acid and diluted to 20 ml. The activity in both solutions was then determined by counting. The results showed that over 70% of the indium added had been collected by the oxide and almost none remained in the supernatant liquor. The experiment was then repeated with a relatively high concentration of cadmium instead of indium, but this time the zinc oxide was dissolved in hydrochloric acid and polarographed. No cadmium step was obtained indicating that the method was satisfactory for separating indium from zinc chloride solution containing cadmium.

It was next shown that the shaking procedure could be replaced by stirring the solution with 0.1 g zinc oxide for 10 min, when recoveries of better than 95% of added indium were obtained from 1 g samples of zinc which had been dissolved in hydrochloric acid, adjusted to pH 2.0 with N sodium hydroxide and diluted to 20 ml.

The method was therefore extended to full sensitivity as follows: 12.5 g zinc oxide was dissolved in hydrochloric acid, 2 drops of cresol red indicator were added and N sodium hydroxide run in until the colour of the solution changed to yellow. 0.5 g zinc oxide was added and the solution then stirred mechanically for 10 min. The oxide was filtered off, dissolved in hydrochloric acid and, if radio-active indium had been added, diluted to 20 ml and counted. If non-active indium had been used, the solution was evaporated to dryness and the residue dissolved in the base electrolyte suggested by MILNER[4] (1 ml 5N hydrochloric acid, 0.5 ml hydrazine hydrochloride, 0.5 ml 60% sodium formate and 0.5 ml 2% starch solution) and polarographed.

Recoveries by counting were all better than 95% and those by polarography gave a good linear concentration-step height relationship as shown in Fig. 1.

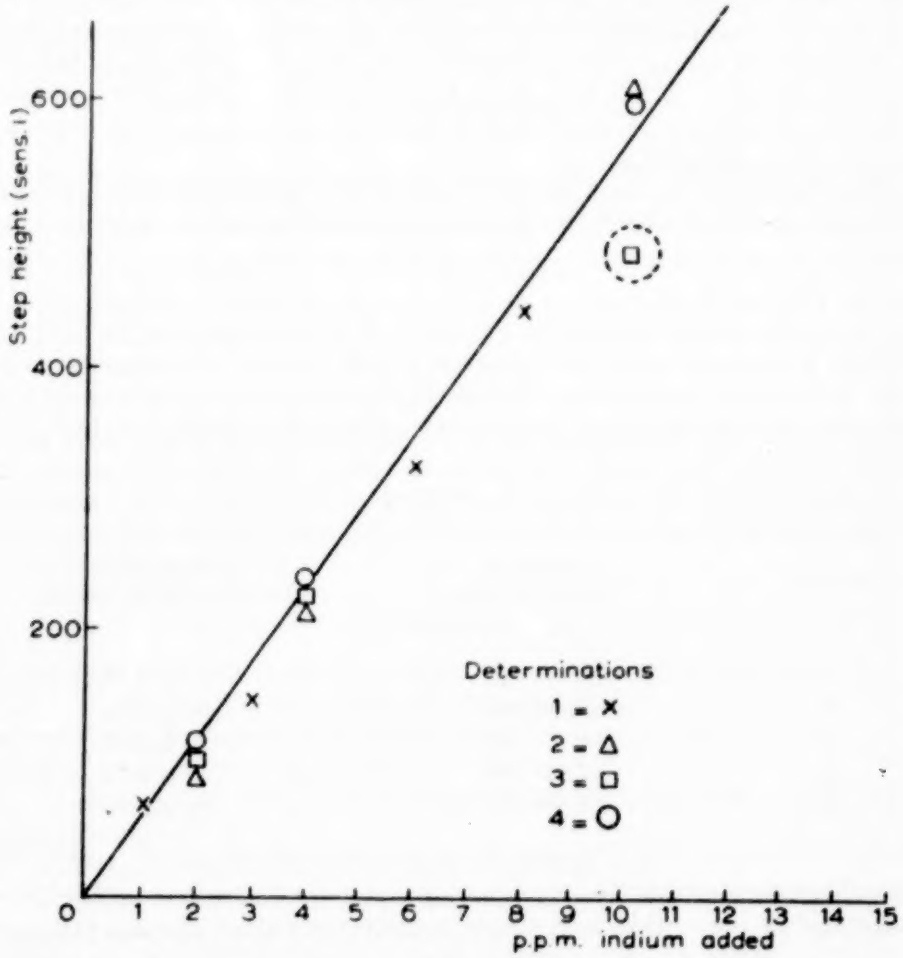

Fig. 1.

The pH of the filtrate from the above separation was always found to be 4.95 ± 0.1. It was therefore concluded that the indium is separated by precipitation as $In(OH)_3$ and the procedure produces conditions which favour this selective precipitation.

Attempts to employ this procedure for mazak alloys were disappointing. The high aluminium contents of these alloys (about 4%) caused difficulties as this element was precipitated with the indium and its gelatinous nature made filtration exceedingly slow and caused heavy contamination by adsorbed ions. Attempts to keep the alumi-

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nium in solution at pH 4.95 with fluoride were only partially successful and it was impossible to finish in the volume of 2.5 ml used above. Citrate was also tried as a complexing agent, but the indium did not precipitate in the presence of this reagent.

The above results showed that the above procedure was not applicable when significant amounts of aluminium (above 0.01%) were present, but in other cases it provided a rapid and sensitive method for the determination of indium. It was therefore incorporated into a method, given below, for alloys of appropriate constitution.

METHOD

Place 10 g of the alloy sample (as turnings or drillings) in a 400 ml beaker and add 45 ml 10*N* hydrochloric acid. Add 2 drops of cresol red and run in *N* sodium hydroxide until the solution is just yellow.

Add 0.5 g zinc oxide powder and stir the solution mechanically for 10 min. Filter through a Whatman No. 541 filter paper and wash the beaker and precipitate three times with water.

Spot the filter paper with 10*N* hydrochloric acid so that the precipitate is completely dissolved and collect the solution in a 250-ml beaker. Wash the paper with water and add the washings to the solution in the beaker. Evaporate just to dryness, cool and dissolve the residue in 1.00 ml 5*N* hydrochloric acid. Add 0.50 ml 20% hydrazine hydrochloride, 0.50 ml 10*M* sodium formate and 0.50 ml 0.2% starch solution. Heat to 60°C, cool and transfer to a polarographic cell.

Deoxygenate the solution for 10 min by bubbling hydrogen or nitrogen through it and record a polarogram over the range —0.375 to —0.75 V on "quarter voltage"*, using the mercury pool as anode. Measure the height of the step due to indium which occurs at —0.53 V and note the sensitivity setting of the polarograph.

Obtain the indium content of the sample by means of the calibration graph obtained as described below, making an appropriate correction for the sensitivity value employed.

Calibration

Dissolve 62.5 g pure zinc oxide powder in 155 ml 10*N* hydrochloric acid, add 2 drops cresol red and run in *N* sodium hydroxide until the solution is just yellow. Transfer to a 500-ml calibrated flask and make up to volume with water. Divide the solution into five 100-ml aliquots, each in a 400-ml beaker and add standard indium solution** as shown in Table I below.

TABLE I

Solution	*Standard indium solution*	*Corresponding indium content (sample)*
1	0.00 ml	0 p.p.m.
2	0.40 ml	2 p.p.m.
3	1.00 ml	4 p.p.m.
4	2.00 ml	8 p.p.m.
5	5.00 ml	20 p.p.m.

Carry out the collection procedure and polarography as described in the method and plot a graph of step height (after correction to a single sensitivity value) against p.p.m. indium.

TESTS OF THE METHOD

No zinc alloys with low aluminium content and containing indium were available. The method was therefore tested by determinations carried out on solutions of AnalaR zinc oxide and pure zinc metal to which relatively high concentrations of copper and lead had been added in addition to standard amounts of indium. The recoveries are given in Table II below.

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* "Quarter voltage" refers to a setting of the polarograph such that only one quarter of the normal potential difference is applied to the polarizing potentiometer. This has the effect of "stretching out" the step over the record, making it more easily measurable.

** The standard indium solution is prepared as follows. Dissolve 0.0121 g pure indium oxide, or 0.010 g pure indium metal in 5 ml 10*N* hydrochloric acid. Transfer the solution to a 250-ml calibrated flask and make up to volume with water.

TABLE II

Sample		*Indium (p.p.m.)**	
		added	*found*
AnalaR zinc oxide	1	2	1.9
	2	4	4.4
	3	10	9.5
	4	20	20.6
Pure zinc metal	1	2	2.3
	2	4	4.3
	3	10	11.2
	4	20	21.0

* These quantities are calculated on the original sample weight

CONCLUSIONS

It was concluded from this work that, although the method described above was suitable for zinc alloys of low aluminium content, it could not be applied to mazak alloys. The study of the remaining line of approach; the use of an iodide base electrolyte was therefore undertaken. This work will be described in Part III of this series[8].

SUMMARY

Studies of the application of an 8-hydroxyquinoline extraction and of a zinc oxide "collection" procedure for the separation of trace amounts of indium from zinc alloys are described and discussed. A combination of radio-chemical and polarographic determinations were employed for this work. A polarographic method for the determination of indium in zinc and in zinc alloys of low aluminium content is presented.

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THE POLAROGRAPHIC DETERMINATION OF INDIUM IN ZINC-BASE ALLOYS

III. THE DETERMINATION OF INDIUM IN ZINC AND IN "LEAD-FREE" ZINC ALLOYS

by

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INTRODUCTION

In previous papers in this series, a rapid method (employing cathode ray polarography) for the determination of indium in zinc alloys, including mazak, has been presented[1] and further work leading to a method for the determination of this element in aluminium-free zinc alloys has also been described[2]. Since this method was not applicable to mazak alloys (aluminium content about 4%), further studies were made with the object of developing a method applicable to these alloys which could be carried out by conventional polarography. The work described in this paper is concerned with the use of an iodide base electrolyte.

It has been reported in the literature[3] that the half-wave potential of cadmium in N potassium iodide is —0.74 V *versus* S.C.E. That of indium in 0.1N potassium iodide is given as —0.53 V *versus* S.C.E.[4] Separation of the two steps is therefore possible in an iodide medium, but, as lead is also complexed by iodide, it appeared probable that this element would interfere if present in the sample. This was supported by the theoretical considerations described below.

The standard electrode potential for the reaction $PbI_2 + 2\,e^- \rightleftharpoons Pb + 2\,I^-$ is reported[5] as: $E^\circ = -0.611$ V *versus* S.C.E. (+0.365 V *versus* N.H.E., American sign convention). It was also calculated from thermodynamic data that for:

$$PbI^+ + 2\,e \rightleftharpoons Pb + I^-$$
$$E^\circ = -0.556 \text{ V } \textit{versus} \text{ S.C.E.}$$

Interference of lead with the indium step therefore appeared certain on grounds of half-wave potential, irrespective of the complex present, provided that the solubility products allowed sufficient lead to remain in solution. K for the reaction:

$$PbI_2 \rightleftharpoons Pb^{+2} + 2\,I^-$$

was calculated from thermodynamic data to be $8.3\cdot10^{-9}$. Therefore the concentration of lead in N iodide solution is very small ($3.3\cdot10^{-8}M$) and negligible compared with the indium concentration desired to determine.

In the case of the reaction:

$$PbI^+ \rightleftharpoons Pb^{+2} + I^-$$

K was calculated to be $3.5\cdot10^{-2}$. In concentrated solutions of iodide the complex $Pb\,I_3^-$ exists. K has been given by KORENMAN[6] as $3.6\cdot10^{-6}$. Therefore the presence of either of these species will increase the lead concentration in solution and variation of the

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iodide concentration in either direction will not serve to decrease it. It was, however, considered that this line of approach was sufficiently promising to merit practical investigation.

EXPERIMENTAL AND DISCUSSION

AnalaR zinc oxide was used as the source of zinc for these experiments and "specpure" indium oxide was used as the source of indium. All polarography was carried out at 25° and *versus* the mercury pool anode. The three polarographs mentioned in Part II of this series[2] were employed. All potentials are quoted on the European sign convention. On this convention the saturated calomel electrode (S.C.E.) has been taken as +0.246 V *versus* the normal hydrogen electrode (N.H.E.).

Polarography was first carried out on solutions of cadmium and indium in 0.1*N* potassium iodide solutions. The half-wave potentials obtained were —0.410 V and —0.240 V *versus* the mercury pool respectively. The pool potential was found to be —0.234 V *versus* S.C.E. so that these values are equivalent to —0.644 V *versus* S.C.E. for cadmium and —0.474 V *versus* S.C.E. for indium. The agreement with previous values[3] is therefore poor.

Solutions of zinc chloride, 0.5*M* with respect to potassium iodide and containing lead were next prepared and polarographed. The results showed that the lead step height remained almost constant despite wide variations of lead concentration. This height was disappointingly large, being approximately equivalent to that given by 20 p.p.m. of indium. Cooling the solutions in ice, followed by rapid filtration failed to reduce this height.

Removal of residual lead by precipitation as sulphide was next attempted. From the solubility products of lead and zinc sulphides it was calculated that, since the concentration of sulphide ion in 0.25*M* hydrochloric acid saturated with hydrogen sulphide is known to be $1.7 \cdot 10^{-22}M$, the concentration of lead remaining in solution should be $2 \cdot 10^{-6}M$, while that of zinc could be as high as 5.5*M*. Solutions of zinc chloride containing lead were therefore prepared and saturated with hydrogen sulphide. They were then evaporated, filtered, made up to standard volume and polarographed. The results showed that little removal of lead had been accomplished and further experiments were therefore conducted using cadmium and mercury as carriers and at pH values varying from 0.5 to 3.4. The removal of lead was slightly better, but was still not satisfactory.

It was concluded from the above that, although this procedure could provide a rapid method for the determination of indium when lead was either absent from the sample, or was present only in amounts which were small compared with the concentration of indium, the method would not be generally applicable to mazak alloys (lead up to 50 p.p.m.[7]).

A typical polarogram obtained from a solution 0.1*N* with respect to potassium iodide and of low lead content is shown in Fig. 1. It should be noted that the cadmium step has a maximum on it and this was found to be usually the case in iodide solution. Simultaneous determination of this element is, therefore, not possible. On cathode ray polarography of a similar solution, this maximum was not observed, but a maximum appeared on the lead peak.

In the method given in detail below, a procedure is included for determining the amount of lead present in the alloy sample. This involves dividing the solution into

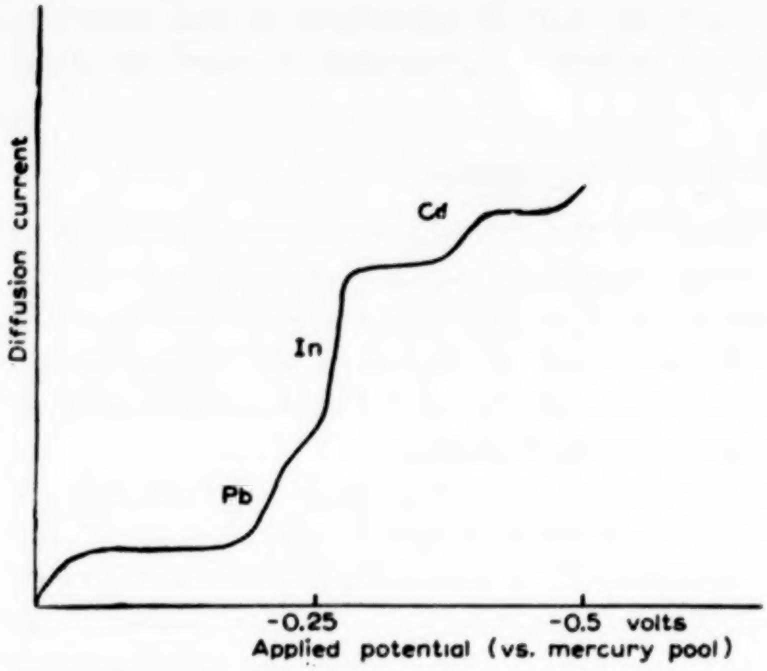

Fig. 1. Lead, indium and cadmium in 0.1*N* potassium iodide.

two aliquots and carrying out polarography on one in the presence of chloride alone. The steps obtained for lead and copper may be used for the determination of these elements, but it should be noted that in the case of samples of high lead content, low results for lead may occur, due to the insolubility of lead chloride.

METHOD

Place 10 g of the alloy (as drillings or turnings) in a 400-ml beaker and add 45 ml 10*N* hydrochloric acid. When almost all the alloy has dissolved, heat the solution and add 100 volume hydrogen peroxide dropwise until dissolution is complete. Evaporate the solution to a volume of about 15 ml, transfer to a 25-ml stoppered measuring cylinder and make up to 18.0 ml with water.

Transfer 9.0 ml of the solution to a 10-ml stoppered measuring cylinder and make up to 10.0 ml with water (Solution A). To the remaining 9 ml of solution add 1.0 ml 5*M* potassium iodide solution (Solution B).

Transfer an aliquot of solution A to a polarographic cell and deoxygenate for 10 min by bubbling hydrogen or nitrogen through it. Record a polarogram over the range −0.25 to −0.75V on "quarter voltage" (Note 1), using the mercury pool as anode. The absence of a step of half-wave potential −0.45 V indicates the absence of lead. If a small step is obtained, measure its height, D_1.

Transfer an aliquot of solution B to a polarographic cell and deoxygenate as described above. Record a polarogram over the range 0.0 to −0.375 V on "quarter voltage" (NOTE 1), using the mercury pool as anode. Measure the height, D_2, of the step which occurs at −0.23 V.

Correct the step heights, D_1 and D_2, to values obtainable on a common sensitivity setting of the polarograph (NOTE 2). Call the new heights D_3 and D_4. Calculate the indium content of the sample from the expression:

$$\text{p.p.m. indium} = F\,(D_4 - D_3)$$

where F is the calibration factor.

Calibration

Blank determination. Dissolve 12.5 g pure zinc oxide in 40 ml 10*N* hydrochloric acid. Proceed as described in the method and let the two corrected step heights obtained, which correspond to D_3 and D_4, be a_1 and a_2 respectively.

Calibration. Dissolve 12.5 g pure zinc oxide in 40 ml 10*N* hydrochloric acid and add 2.5 ml of standard indium solution (NOTE 3). Proceed as described in the method and let the two corrected step heights obtained, which correspond to D_3 and D_4, be b_1 and b_2 respectively.

Calculate the calibration factor, F, from the expression:

$$F = \frac{10}{(b_2 - b_1) - (a_2 - a_1)}$$

Notes

1. "Quarter voltage" refers to a setting of the polarograph such that only one quarter of the normal potential difference is applied to the polarizing potentiometer. This has the effect of "stretching out" the polarogram over the record, making it more easily measurable.

2. It is often convenient to choose the maximum sensitivity setting of the polarograph as the standard value to which all values of step heights are corrected. The actual value chosen is, however, unimportant, provided that it is used for all corrections both in the determination and the calibration.
3. The standard indium solution is prepared as follows. Dissolve 0.0121 g pure indium oxide, or 0.010 g pure indium metal in 5 ml 10N hydrochloric acid. Transfer the solution to a 250-ml calibrated flask and make up to volume with water.

TESTS OF THE METHOD

Tests of the method given above were made by carrying out determinations on solutions of pure zinc oxide and of mazak alloys of approximately the composition described in an earlier paper[1]. The mazak alloys employed were specially chosen for their negligible lead content. The results obtained with each sample solution, to which standard amounts had been added, are given in Table I below.

TABLE I

Sample		*Lead content (p.p.m.)**	*Indium (p.p.m.)**	
			Added	*Found*
Zinc oxide	1	20	6	7.0
	2	20	10	10.2
	3	20	20	20.2
Mazak alloy	1	—	10	8.8
	2	—	10	11.0
	3	—	20	19.4
	4	—	20	20.6

* These quantities are calculated in the original sample weight.

CONCLUSIONS

It was concluded from the work described in this paper that, although the method developed was suitable for zinc alloys of low lead content, it could only be applied to a few mazak alloys. Since no fresh lines of approach to this problem were known, it was decided to attempt to develop a procedure based on the zinc oxide "collection" method already described[2]. Such a method would involve a time-consuming separation procedure owing to the high aluminium content but this appeared to offer the only alternative to the method employing cathode ray polarography[1]. The development of this method will be described in Part IV of this series of papers.

SUMMARY

The use of a potassium iodide base electrolyte for the separation of the polarographic steps due to indium and cadmium is discussed and theoretical data relating to the interference of the step due to lead with that due to indium are presented. An experimental study is given together with details of the attempted removal of lead interference. A method is presented for the polarographic determination of indium in zinc alloys, applicable when the lead concentration is small compared with that of indium.

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THE POLAROGRAPHIC DETERMINATION OF ALUMINIUM*

I. GENERAL INTRODUCTION. POLAROGRAPHY OF SOLOCHROME VIOLET R.S. IN THE PRESENCE OF ALUMINIUM

by

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INTRODUCTION

General

A survey of the literature reveals a lack of satisfactory methods for the determination of microgram quantities of aluminium, especially when interfering elements are present. Many methods are based on the formation of coloured lakes by combination with an organic reagent such as ammonium aurincarboxylate, alizarin S, eriochrome cyanin or heamatoxylin. The composition of these lakes is uncertain, but they have been regarded[1] either as internal complexes of aluminium, which exist in colloidal solution, or as a colloidal aluminium hydroxide on which the organic compound is adsorbed. Determinations based on these lakes all suffer serious interference from iron. The determination involving haematoxylin has been extensively studied in this Department[2,3] since the bleaching, by fluoride, of the coloured lake has been used to determine fluorine. Another colorimetric method involves the formation of aluminium hydroxyquinolate, followed by coupling with a diazo compound to form an arylazo dye[4]. The colorimetric determination of aluminium has been the subject of a comparative survey by SCHAMS[5]. Nephelometric and turbidimetric methods involving cupferron have also been reported[6].

Fluorimetric methods employing morin[7], quercitin[8] and diortho-hydroxyazo dyes[9] have been described. These are very sensitive, but are somewhat unreliable. They suffer considerably from the presence of many interfering ion species.

In general spectrographic techniques are not very successful, owing to the refractory nature of aluminium oxide.

Interference from a large number of elements, suffered by the above methods, makes separation prior to determination essential. Most of the separation techniques described in the literature are not easily applicable when aluminium is present in trace amounts.

The following are most commonly applied:

1. Precipitation by ammonium hydroxide in the presence of ammonium chloride. This separates aluminium from magnesium and the alkaline earth metals, but the strong adsorption of other elements on the precipitated alumina makes it unsatisfactory for microgram quantities. In addition a carrier, usually iron, must be employed to ensure complete precipitation and this must subsequently be removed before the final estimation.

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2. Precipitation with cupferron in sulphuric acid separates aluminium from iron and certain other elements. The iron cupferrate may be extracted with ether.
3. Extraction with 8-hydroxyquinoline in chloroform at pH 4.5 separates aluminium from beryllium, magnesium and the alkaline earth metals. Many other metals including iron, however, are also extracted.
4. Electrolysis at stirred mercury cathode is very useful for removing a large number of interfering elements from aluminium solutions. Elements not removed include beryllium, magnesium and the rare and alkaline earth metals. This technique will be discussed in greater detail later.

In view of the unsatisfactory nature of the existing techniques, work was undertaken to develop a more suitable method for the determination of microgram amounts of aluminium, which would avoid complicated chemical separations. A primary objective was the determination of small amounts of aluminium present as impurity in beryllium metal.

The polarography of aluminium

The first reported study of the polarographic behaviour of aluminium was that of PRAJZLER[10] who obtained a fairly well-defined step at a halfwave potential of —1.75 V *versus* S.C.E. in 0.05*N* barium chloride. ISHIBASHI AND FUJINAGA[11] used lithium hydroxide at pH 4 (unbuffered) as the base electrolyte and reported a value of —1.76 V *versus* S.C.E. More recently they have stated[12] that the accurate value of half-wave potential is —1.758 ± 0.008 V *versus* S.C.E. These values are lower than would be expected from the standard electrode potential for the couple

$$Al^{+3} + 3e^- \rightarrow Al$$

given by LATIMER AND GREENFELDE[13] as —1.90 V *versus* S.C.E. (1.66 V *versus* N.H.E. American sign convention). This figure is considered to be unreliable.

Direct polarography has been employed in a number of determinations[14,15], but the critical conditions required seriously limit its use. These conditions are outlined below.

The highly-negative half-wave potential of aluminium causes it to be preceded by the hydrogen reduction wave and it only just precedes the discharge potentials of calcium, barium, magnesium, beryllium and the alkali metals. The aluminium step is not normally measurable in the presence of large concentrations of these elements. The fact that the hydrogen wave precedes that of aluminium is not important provided that the hydrogen ion concentration does not exceed that of aluminium. Under this condition the aluminium step is well separated, but if the hydrogen ion concentration is high, it is completely masked.

The minimum tolerable pH for the formation of a satisfactory aluminium step is about 3; this value needs to be increased with decreasing aluminium concentration. On the other hand, however, the pH value of the solution must not rise above that of the natural pH resulting from the hydrolysis of aluminium or precipitation will occur. SAMERANO AND RONCHI[16] state that the pH of pure solutions of aluminium chloride depend on the molar concentration *c* according to

$$\text{pH} = 2.65 - 0.54 \log c$$

which gives a value of 3.73 for the pH of $10^{-2}M$ aluminium chloride and 4.81 for a $10^{-4}M$ solution.

These considerations indicate that the pH range for the satisfactory polarography of aluminium is very limited and critical. It is unlikely to be obtainable under routine analytical conditions. In addition the interference of beryllium when present in significantly larger concentrations, rendered the development of a simple method for the determination of aluminium in beryllium impossible.

The indirect method PARKES AND LYKKEN[17] was considered. In this method the aluminium is precipitated with 8-hydroxyquinoline and the excess of this reagent is then determined polarographically. It appeared that this would not be very satisfactory in view of the limitations imposed by the necessity of ensuring the absence of all other ion species which would also combine with the reagent under the prescribed conditions.

A further method, developed by WILLARD AND DEAN[18] appeared to be much more promising. In this, the modification, by aluminium, of the polarographic reduction of a diortho-hydroxyazo dye is employed. The method is based on the fact that a solution of the azo dye is reducible at the dropping mercury electrode yielding a polarographic step of half-wave potential —0.2 V *versus* S.C.E., the exact value being dependent on the pH. In the presence of aluminium at pH 4.6 the height of the step at this potential is reduced and a second step, with a half-wave potential of about 0.2 V more negative, appears. The total height of the two steps is equal to the height of the original step (dye alone) and the second step height is directly proportional to the aluminium concentration. The method was stated to be very sensitive and to suffer no interference from beryllium or the alkaline earth metals.

In view of the promising nature of the azo dye method some preliminary experiments were made to check the results of other authors and the work was then confined to a study of the dye Pontachrome Violet S.W. WILLARD AND DEAN have recommended this dye in preference to other similar compounds which give similar reactions on account of its greater solubility in water. The equivalent British material is Solochrome Violet R.S. (colour index No. 169).

Concurrently with this work an investigation into the application of the method to the indirect determination of microgram amounts of fluoride was made. The results of this have been published elsewhere[19,20].

EXPERIMENTAL

General

Unless otherwise stated, all polarography was carried out at 25° on a Cambridge direct writing polarograph. All half-wave potentials are given in the European sign convention and *versus* the mercury pool anode. On this convention the saturated calomel electrode (S.C.E.) has been taken as + 0.246 V *versus* the normal hydrogen electrode (N.H.E.)

Preliminary work

Polarography of aluminium in barium chloride. A number of determinations were made with standard solutions of aluminium in solutions of barium chloride at various concentrations and at various pH values. The steps obtained were generally well-formed, but the aluminium step was often imperfectly separated from those due to hydrogen and barium. The half-wave potential of the aluminium step was about — 1.85 V. A typical step is shown in Fig. 1.

These results confirmed that a determination of this type would not be of use for trace amounts of aluminium in beryllium and no further study was, therefore, made.

Polarography of aluminium in concentrated calcium chloride solution. During some previous work on the polarographic behaviour of certain elements in 5*M* calcium chloride solution[21] steps due to aluminium, present as impurity in the calcium chloride, were occasionally encountered. Solutions of aluminium in this medium were polarographed on a Randles-type cathode ray polarograph[22,23] and, although well-formed steps were generally obtained, the results were disappointingly unpredictable. Further study was, therefore, deferred and will be reported later in this series.

Polarography of solochrome violet R.S. in the presence of aluminium. For this part of the investigation, the procedure of WILLARD AND DEAN[18] was employed. A 100 μg/ml standard aluminium solution was prepared by dissolving 0.4203 g of AnalaR ammonium aluminium sulphate in 50 ml water containing 3 ml 60 % perchloric acid and making up to 250 ml with water. Aliquots of this solution were placed in a series of 50-ml graduated flasks so that they contained 0, 50, 100, 150, 250 and 300 μg of aluminium respectively. Each flask was then treated as follows: 10 % sodium hydroxide was added dropwise until the solution was just alkaline to methyl red. 2.5*N* perchloric acid was then added until the solution was just acid. 2 ml of the perchloric acid, 4 ml of 2.5*N* ammonium acetate and 20 ml of 0.50 % (w/v) solochrome violet R.S. solution were then added and the solution made up to volume with water. After immersion in a water bath at 60–70° for five min, the flasks were cooled and aliquots were deoxygenated and polarographed using the mercury pool as anode.

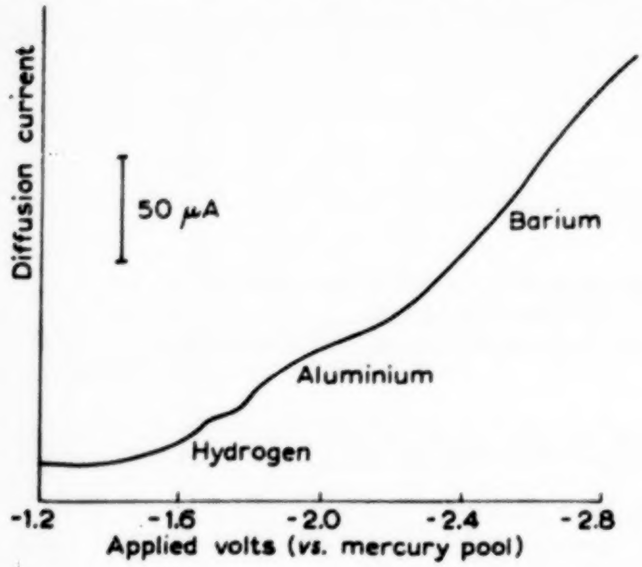

Fig. 1. Polarography of aluminium in barium chloride. $1.48 \cdot 10^{-3} M$ aluminium in $0.05 M$ barium chloride. pH 2.3.

The results obtained are given Table 1 and typical steps in the presence and absence of aluminium are shown in Fig. 2.

The final pH values were 4.5-4.6 and the half-wave potentials were found to be —0.46 and —0.64 V respectively (*versus* mercury pool)

TABLE I

Concentration of aluminium (μg/ml)	*Step height (arbitrary units)*	*Step height per μg g/ml*
0	0	—
1	6.5	6.5
2	15.0	7·5
3	21.5	7·2
5	35·5	7·1
6	41·5	6.9

Interfering species

The interference of a number of common ion species with these satisfactory results was next studied. A series of 50-ml graduated flasks was charged with 100 μg aluminium and varying amounts of the ion species to be studied. The flasks were then treated as in the above section. Similar determinations were also made in the absence of aluminium. The results obtained are listed below.

Beryllium, boron, calcium, magnesium and zinc gave no serious interference in excesses up to one hundredfold over aluminium in the case of boron and beryllium, and up to one thousandfold in the case of calcium, magnesium and zinc. The dye step was unaffected by these ions in the absence of aluminium.

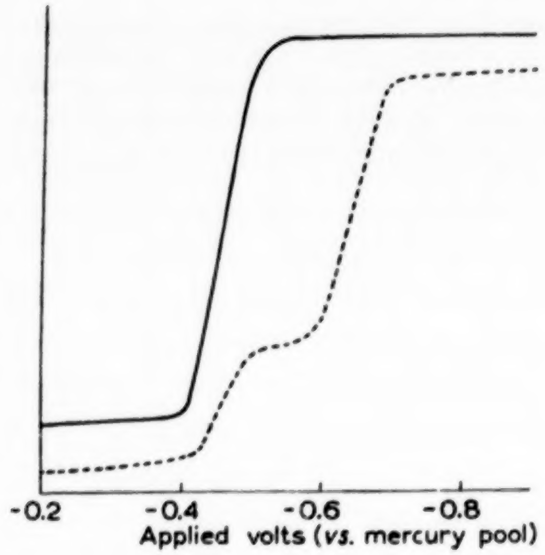

Fig. 2. Polarography of solochrome violet R.S.
———————— aluminium absent,
- - - - - - - - - - - in presence of 5 μg/ml aluminium.

Antimony and lead both enhanced the aluminium dye step at all concentrations. Steps were observed in the absence of aluminium at a half-wave potential of —0.625 V in the case of antimony and —0.66 V in the case of lead. The results indicated that the interference was more serious when the antimony was in the trivalent state than when it was pentavalent.

Arsenic in the pentavalent state had no effect up to an excess of one hundredfold. In the trivalent state the interference took the form of a very slight decrease in the aluminium-dye step height. The half-wave potential also became slightly more positive.

Cobalt, thorium, titanium(IV), vanadium(V) and zirconium all enhanced the aluminium–solochrome violet step. In the case of thorium, however, an appreciable effect was only evident when its concentration was ten times that of aluminium. Steps due to titanium(IV) and vanadium(V) were found to be at the same half-wave potential as the aluminium, but they were too poorly defined to have any value for analytical purposes.

Iron(III) and nickel, at all concentrations, caused an increase in the aluminium-dye step height. The half-wave potentials also shifted to more negative values. In the presence of iron the solution became brownish, in contrast with the bright red colour associated with the presence of aluminium alone. Both elements yielded well-formed steps in the absence of aluminium, the half-wave potential of the iron–dye step occurring at —0.76 V and that of the nickel at —0.75 V. The relationship between step height and concentration was linear in the case of nickel and could be employed, if desired for the determination of this element. The step due to iron was not quantitative under the conditions employed. A typical wave obtained with a solution containing iron, aluminium and solochrome violet R.S. is shown in Fig. 3.

Molybdenum caused a slight depression of the aluminium step height when these two elements were present in approximately equal concentrations. At higher molybdenum concentrations a marked depression occurred and this was followed by a large maximum. On suppression of this maximum with proteose peptone, three steps were obtained at half-wave potentials of —0.465 V (free dye), —0.555 V (dye–aluminium) and —0.82 V. In the absence of aluminium, steps at —0.465 and —0.82 V only were obtained.

Cadmium produced a step immediately following that of the aluminium–solochrome violet R.S. and caused a slight depression of the latter. In pure acetate buffer of pH 4.6 (aluminium and solochrome violet not absent) the cadmium step was obtained at the

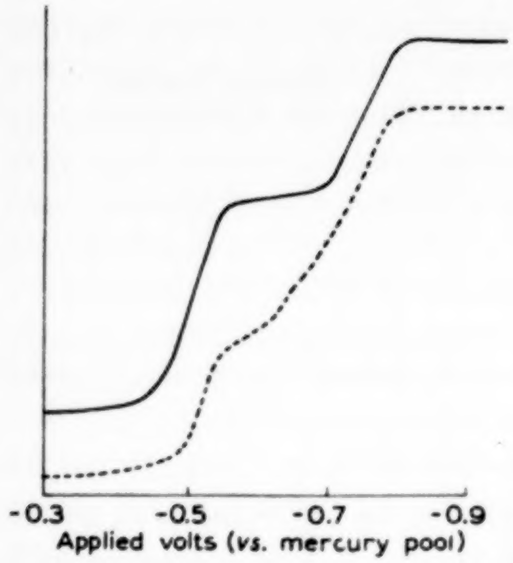

Fig. 3. Solochrome violet R.S. in the presence of ferric iron.
——— 4 µg/ml ferric iron,
- - - - - 4 µg/ml ferric iron + 5 µg/ml aluminium.

same half-wave potential as in the presence of aluminium and solochrome violet R.S. (—0.8 V).

Copper and tin both caused precipitation from the aluminium-dye solution. In the case of copper, a brownish precipitate formed when the copper concentration exceeded that of aluminium and low aluminium recoveries were obtained under these conditions. In the case of tin, the precipitate appeared to be of tin itself, probably as stannate.

Manganese did not interfere up to a concentration five hundred times that of aluminium. Above this, a slight depression in the height of the aluminium-dye step was noted.

Phosphorus in the pentavelent state gave an effect similar to that of antimony, but in this case significant depression occurred when the phosphorus : aluminium concentration ratio was 30 : 1.

Uranium caused no interference when its concentration was less than five times that of aluminium. Above this figure, the dye and dye-aluminium steps were distorted by a large pre-wave which enhanced their step heights and caused the half-wave potential of the dye-aluminium step to shift to a more negative potential. In the presence of the acetate buffer alone, uranium gave a step at —0.7 V.

Fluoride, citrate and oxalate all reduced the height of the aluminium step by an amount that was a linear function of the concentration of the anion. As mentioned earlier, this effect has been employed in these laboratories as a means of determining trace amounts of fluoride and has been fully reported elsewhere[19,20]. Similar procedures could be used for the determination of microgram amounts of citrate and oxalate ions and it is considered that the oxalate method, although not specific, would compete in sensitivity with the polarographic method involving precipitation with europium[24]. A typical set of results for citrate is shown in Table II.

Anode pool potential

Finally the anode pool potential was measured so that direct comparison of half-wave potential values could be made. One of the aluminium-solochrome violet solutions already employed for polarography was allowed to stand for a few minutes with a potential of 2 V applied between the pool and the dropping mercury cathode. A saturated calomel electrode was then connected via a salt bridge and the pool potential was measured by means of a Cambridge pH meter set to read millivolts. The measured pool potential was + 0.279 V *versus* S.C.E.

TABLE II

Citric acid concentration (µg/ml)	*Step height* (4 µg Al/ml)*	*Step height depression per µg citric acid/ml*
0	36.5	—
1.28	35.0	1.17
2.56	34.0	0.98
3.84	32.0	1.17
7.68	28.0	1.11
15.36	20.0	1.07

* Step heights are in arbitrary scale divisions recorded on sensitivity setting 1/20 on the Cambridge Direct Writing Polarograph employed.

DISCUSSION

Taking the activity coefficient of 0.05M barium chloride as 0.56[25] the pool potential in this solution is calculated to be + 0.098 V *versus* S.C.E. Our measured half-wave potential for aluminium (—1.85 V) is therefore equivalent to —1.75 V *versus* S.C.E. This is in good agreement with other values[10–12]. Fig. 1 shows that the aluminium step is closely preceded and followed by two other steps, assumed to be due to the reduction of hydrogen ion and of barium respectively.

Assuming the reduction of barium at the dropping mercury electrode to be

$$Ba^{+2} + 2e^{-} \rightarrow Ba\ (Hg)$$

the standard electrode potential is calculated from thermodynamic data to be —3.15 V *versus* S.C.E., giving a calculated half-wave potential of —2.17 V *versus* S.C.E. The barium step should, therefore, not interfere with that of aluminium. It will be noted from Fig. 1 that the barium step is very "drawn out" and has an apparent half-wave potential of a more negative value than that calculated. This is, of course, to be expected since it is acting as the base electrolyte and its reduction is therefore not entirely diffusion-controlled.

The magnitude of interference with the aluminium step by the hydrogen reduction is a function of pH. Table III shows calculated half-wave potentials and step heights for hydrogen at various pH values.

TABLE III

pH	*Hydrogen ion wave*	
	Half-wave potential (V versus S.C.E.)	*Step height* (arbitrary units)*
0	−1.48	146,000
1	−1.51	14,600
2	−1.54	1460
3	−1.57	146
4	−1.595	14.6

* All step heights are corrected to the sensitivity setting 1/30 on the Cambridge Polarograph employed. On this setting $10^{-3}M$ aluminium gave a step height of 320 scale divisions.

The above values show that at values below pH 2 the hydrogen step is inconveniently large and even at pH 3 it is about half the height of the step due to $10^{-3}M$ aluminium. The natural pH of $10^{-3}M$ aluminium chloride calculated by the equation of SAMERANO AND RONCHI[16] is 4.27 and within the pH range 3 to 4 mutual interference between the hydrogen and aluminium waves occurs. For minimum interference the pH range must be limited to 3.5 to 4 and from similar considerations this range becomes 4 to 4.5 in

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the case of $10^{-4}M$ aluminium. In the latter case the half-wave potential of the hydrogen reductions is such that serious masking of the aluminium step occurs. It was therefore obvious that in a method based on this procedure, not only would the conditions be very rigid, but they would have to be varied according to the concentration of aluminium present. Such a method would not be applicable to concentrations less than $10^{-3}M$ aluminium.

The results obtained by us using the WILLARD AND DEAN technique[18] were generally in close agreement with those of the authors. A more detailed study of the mechanism of this type of reaction will be presented later in this series.

WILLARD AND DEAN reported half-wave potentials of —0.34 and —0.53 V *versus* S.C.E. for the dye and dye-aluminium steps respectively. Our values of —0.46 and —0.64 V *versus* the mercury pool are equivalent to —0.18 and —0.36 V *versus* S.C.E. Our measured potential of + .279 V *versus* S.C.E. for the mercury pool in the presence of the acetate-perchlorate dye solution (pH 4.6) is close to the standard electrode potential of + 0.264V *versus* S.C.E. quoted by LARSEN AND MACDOUGALL[26] for the reaction

$$Hg_2\,(CH_3CO_2)_2 + 2\,e^- \rightarrow 2\,Hg + 2\,CH_3CO_2^-$$

It appears, from the diagram of the polarographic steps published in their paper, that WILLARD AND DEAN found that the half-wave potential of the free dye was shifted to a value 0.1 V more positive when aluminium was present. They do not comment on this phenomenon and we have not observed it.

The experiments carried out to study the interference of other ion species with the aluminium-dye reaction show that no interference is caused by large excesses of beryllium, boron, calcium, magnesium, manganese and zinc. This method is therefore particularly suited to the determination of trace amounts of aluminium in beryllium, which was the primary object of the present work. The application will be described in Part II of this series[36]. The results obtained in the presence of cobalt, iron, nickel, titanium and vanadium show that these elements also form complexes with solochrome violet R.S. Their half-wave potentials are sufficiently close to cause enhancement of the aluminium step. This is mentioned by WILLARD AND DEAN[18] and complexes of similar dyes with cobalt and nickel[27,28] and with vanadium[29] have been described recently. The precipitation by copper is evidently due to the formation of an insoluble complex. Copper-azo dye complexes have been dealt with in a number of papers[30-33] and will be discussed comparatively later. The precipitation with tin seems more likely to be due to coprecipitation with stannate than to complex formation. The step obtained in the presence of uranium gives some indication of complex formation but the pre-step in the aluminium step is thought to be due to interference by the reduction of uncomplexed U(VI) → U(V) at about its normal potential.

The mechanism of the fluoride, citrate and oxalate interference is the reverse of those described above. Here the tendency is to combine with the aluminium in competition with the dye. As already mentioned, this has been used to determine microgram amounts of fluoride[19,20]. The pH used in that work was 3.9 to favour the formation of aluminium fluoride. Similar methods of considerable sensitivity could be developed for oxalate and citrate.

A general study of the interferences does not indicate any general rule by which the possibility of interference by any ion species could be predicted. There seems to be a

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strong tendency for trivalent species to complex, and less tendency for higher valency states. The total absence of complexing by beryllium, zinc and the alkaline earth metals is notable, but this might be peculiar to solochrome violet R.S. as dyes of similar structure have been shown to complex with magnesium[34].

A large number of elements which interfere seriously with the determination may be removed by electrolysis at a stirred mercury cathode. The conditions for this separation will be discussed in Part II of this series[36]. The separation of titanium has been described by MIKULA AND CODELL[35].

No discussion of the structure of the aluminium-dye complex will be attempted here. Further data will be presented and discussed in later papers in this series.

SUMMARY

A survey is made of the methods available for the determination of microgram quantities of aluminium, together with techniques for its separation from interfering ion species. The polarography of aluminium is briefly discussed and a study is reported of a method involving the modification, by this element, of the polarographic characteristics of a diortho-hydroxy azo dye. Interferences from other elements are given in detail and discussed. Means for their removal are suggested.

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THE POLAROGRAPHIC DETERMINATION OF ALUMINIUM*

II. THE DETERMINATION OF MICROGRAM AMOUNTS OF ALUMINIUM IN BERYLLIUM METAL

by

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INTRODUCTION

General

In part I of this series[1] the polarography of aluminium was discussed in detail and an investigation of the method of WILLARD AND DEAN[2] was described. This method is based upon the modification, by aluminium, of the reduction step due to solochrome violet R.S. A study of the interferences of other elements with this method showed that no interference was caused by relatively high concentrations of a number of elements including beryllium. It was therefore decided to use this as a basis for the development of a method for the determination of small amounts of aluminium present as an impurity in beryllium metal.

The beryllium metal to which the method was to be applied was required to have special metallurgical properties. These necessitated a low aluminium content. An upper limit of 500 p.p.m. (0.05%) was specified, but it was hoped that the actual value would be well below this figure. In addition a large number of other trace metals were expected to be present in amounts ranging from 10 to 500 p.p.m. It was therefore necessary that the method should be very sensitive and should be satisfactory in the presence of a number of interfering elements whose concentration might be several times that of the aluminium.

Examination of the results obtained previously[1] indicated that, of the elements which might be present, only iron, lead, copper, antimony, nickel and uranium would interfere. Of these, iron was often present in amounts greater than that specified for the aluminium (500 p.p.m.), while the others were sometimes present in concentrations approaching 100 p.p.m.

It was decided that the most satisfactory procedure would be the complete removal of the interfering elements from the solution prior to the determination of aluminium. Electrolysis at a mercury cathode was considered to be the most promising method of achieving this. The first part of the work covered by this report was therefore concerned with the establishment of the conditions for this electrolysis. The second part was devoted to the application of the solochrome violet method to the determination of aluminium in the presence of high beryllium concentrations.

Unless otherwise stated, all polarography was carried out at 25° on a Cambridge direct writing polarograph and *versus* the mercury pool anode. All half-wave potentials are given on the European sign convention. On this convention, the potential of the saturated calomel electrode (S.C.E.) has been taken as +0.246 V *versus* the normal hydrogen electrode (N.H.E.).

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EXPERIMENTAL

Mercury cathode electrolysis

For this work the apparatus in Fig. 1 was constructed. The size of the glass electrolysis vessel was such that 25 ml of solution could be conveniently electrolysed. The glass stirrer was driven by a small electric motor. The variable potential difference between the electrodes was provided by a potentiometer fed from a 6 V accumulator. A voltmeter with a range of 0 to 10 V and an ammeter with the ranges 0 to 0.1 and 0 to 1 A were also incorporated in the circuit.

A standard solution of aluminium was prepared containing the interfering elements listed above. The method of preparation was as follows. The elements, either in the form of metal or oxide, were dissolved in 10 ml 10*M* hydrochloric acid, to which a few drops of concentrated nitric acid had been added. The solution was evaporated repeatedly almost to dryness with additions of 10*M* hydrochloric acid and was then diluted to about 25 ml with water. 50 ml of 60% perchloric acid was added and the solution evaporated to fuming. After cooling and dilution it was transferred to a 250-ml graduated flask and made up to volume with water. The aluminium concentration of this solution was 400 μg/ml. That of the iron was also 400, while the lead was 200 μg/ml. The concentrations of copper, nickel, antimony and uranium were each 40 μg/ml.

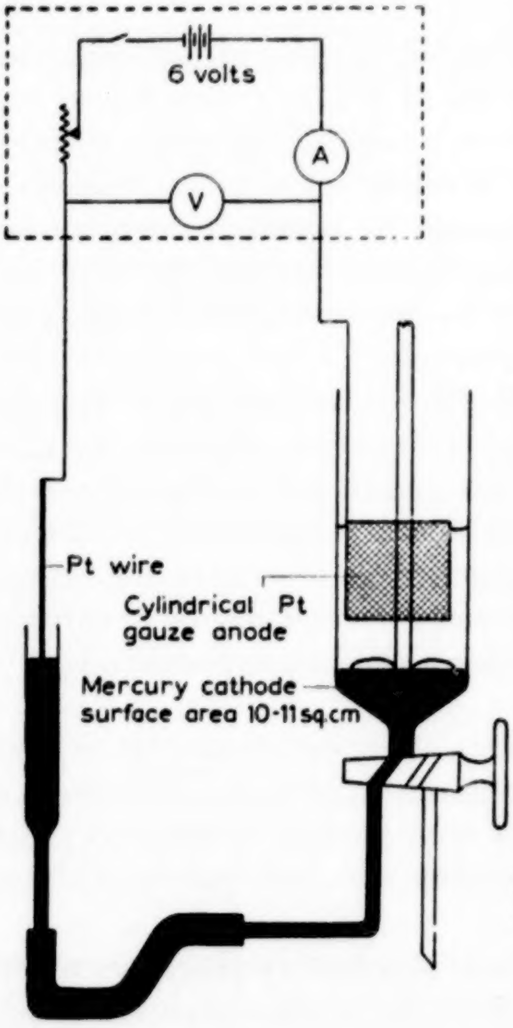
6 volts
A
V
Pt wire
Cylindrical Pt gauze anode
Mercury cathode surface area 10-11 sq.cm

Fig. 1. Mercury-cathode electrolysis apparatus.

5 ml of the prepared solution was placed in a 250-ml graduated flask, 20 ml 60% perchloric acid was added and the flask was made up to volume with water. 25-ml portions of this solution were successively electrolysed under different conditions and the following procedure was applied to each aliquot.

At the conclusion of the electrolysis period the stirrer was stopped and the mercury pool was run out of the vessel while the electrolysing potential was still being applied. 20 ml of the solution was then placed in a 50-ml beaker and evaporated to about 5 ml. After neutralisation to methyl red with 10% sodium hydroxide, the solution was just re-acidified with 2.5*N* perchloric acid and 2 ml of this reagent was added in excess. The solution was transferred to a 50-ml graduated flask, 4 ml of 2.5*N* ammonium acetate was added, followed by 20 ml of 0.05% solochrome violet R.S. solution and the flask was made up to volume with water.

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The series of solutions prepared as described above was heated in a water bath at 70° for 5 min cooled to room temperature, deoxygenated and polarographed. A fuller account of this polarographic procedure is given in Part I of this series[1].

Initial results with solutions electrolysed at currents of less than 50 mA for periods up to 1 h all showed apparent aluminium recoveries of more than 100%. This was shown to be due to incomplete removal of iron and the experiments were therefore repeated with a current of 500 mA for 1 h. Iron was now completely removed while recoveries of aluminium from standard solutions was about 100%. These conditions were therefore adopted for all subsequent work.

Determination of aluminium in the presence of beryllium

A standard beryllium solution was first prepared by dissolving 4 g beryllium metal in about 70 ml 10*M* hydrochloric acid. When dissolution was complete, the solution was evaporated to small bulk and diluted with water. 20 ml 60% perchloric acid was then added and the evaporation repeated. Finally the solution was transferred to a 250-ml graduated flask and made up to volume with water. 25-ml aliquots of this solution were taken with standard amounts of an aluminium solution ranging from 0 to 375 μg of aluminium. They were then electrolysed under the conditions already established.

Attempts to determine aluminium directly in this solution, by the method described above, were unsuccessful. Adjustment of the pH to 4.6 could not be carried out due to the precipitation of beryllium hydroxide and a complicated procedure had to be developed using a pH meter and 30% sodium hydroxide solution. Polarography of the solutions prepared in this way gave the usual two steps, but the total step height was small and salting out of the dye was noted. Moreover the aluminium blank on these solutions was responsible for a large step and, unexpectedly, the increase in step height with added aluminium was only a fraction of that obtainable in the absence of beryllium. Experiments made to study the effect of high beryllium concentrations on the aluminium-dye step height showed that the depressive effects became noticeable above a beryllium-aluminium ratio of 100:1 (400 μg beryllium in the final solution) and that results were meaningless at a ratio of 250:1. Since the full beryllium content of the sample was equivalent to 6400 μg/ml in the final solution, it was evident that the development of a separation procedure was necessary.

Separation of aluminium from beryllium

A study of the literature showed that the procedure most likely to be applicable to the problem was the extraction of the aluminium as the 8-hydroxyquinolate (oxinate) with chloroform at pH about 4.5[3]. It was noted that the iron would also be extracted at this pH, so that the necessity for the electrolysis would still remain. The only alternative separation was that described by PRIBIL AND KUCHARSKY[4] employing ethylenediaminetetraacetic acid, but as this had been developed for traces of beryllium in aluminium, it was thought that it could not be satisfactorily adapted.

A standard solution of beryllium was prepared by dissolving 4 g beryllium metal in 100 ml 60% perchloric acid. The solution was then evaporated to low bulk, diluted with water, transferred to a 250-ml graduated flask and made up to volume. A 25-ml aliquot of this solution was electrolysed at the mercury pool cathode for 1 h at 500 mA. This required an applied voltage of 3.8 V and the cathode potential was measured as —1.71 V *versus* S.C.E.

20 ml of the electrolysed solution were withdrawn, the pH was adjusted to 4.4 with sodium acetate and extraction with four 10-ml portions of 0.2% 8-hydroxyquinoline in chloroform was carried out. The chloroform extracts were then combined and re-

extracted with three 10-ml aliquots of $5N$ nitric acid. The acid solution was evaporated to small bulk and transferred to a Kjeldahl flask. A few drops of $18M$ sulphuric acid were added and the flask was heated until dense fumes were evolved. $16M$ nitric acid was added dropwise and the flask again strongly heated. This addition of nitric acid was repeated twice and, after evaporation to small bulk, a few drops of 60% perchloric acid were added and the solution evaporated to dryness. The residue was treated with 0.5 ml 60% perchloric acid and dissolved in 20 ml water. pH adjustment and polarography (without further electrolysis) was then carried out.

The results obtained with several replicate solutions were all poor. The polarographic steps were distorted and unmeasurable; indicating that even with this vigorous treatment the oxine was not totally destroyed. Experiments were, therefore, made to develop a more satisfactory procedure.

Among the procedures tried for the destruction of the oxine was that of FEIGL AND SCHAEFFER[5], which involved evaporation to dryness, suspension in water and treatment with sulphuric acid, silver nitrate and solid ammonium perchlorate. An alkali fusion at red heat in a silica crucible, after extraction of the chloroform solution with $0.1N$ sodium hydroxide was also attempted and a similar fusion at 700° with sodium carbonate was tried. None was successful.

In view of this more vigorous acid oxidation was employed. The extraction of the oxinate into chloroform and then into nitric acid was carried out as before and the solution was placed in a 100-ml tall-form beaker fitted with a cover glass. 1 ml of 20 vol% hydrogen peroxide was added and the solution was evaporated almost to dryness, while the sides of the beaker were periodically rinsed down with small volumes of $16M$ nitric acid. After cooling, 2 ml of $18M$ sulphuric acid was added and the solution heated until dense fumes were evolved. $16M$ nitric acid was then very carefully added down the sides of the hot beaker, and heating and addition of nitric acid was continued until, on evaporation to dryness the residue was white. During the oxidation it was necessary to make periodic additions of sulphuric acid to replace losses.

It was shown that complete destruction of the oxine took place under these conditions. The procedure was therefore adopted for use in the method detailed later.

Determination of aluminium in beryllium

The recoveries of aluminium obtained in the work described above were of the order of 70%. Experiments were therefore made to increase the efficiency of the method. As a result the following modifications were made:

(1) The pH for the oxine extractions was raised from 4.5 to 5.0.
(2) The mercury cathode electrolysis was carried out on the perchloric acid solution of the residue remaining after the acid destruction of the oxine.
(3) The 0.2% oxine in chloroform was replaced by a 0.8% solution of oxine in 2% acetic acid.

Under these conditions no interference from oxine or iron occurred and recoveries of added aluminium were better than 95% as shown in Table I below. A typical polarogram is shown in Fig. 2.

METHOD

Place 4 g of the beryllium metal sample in a 600-ml beaker, fitted with a cover glass. Add 50 ml water and carefully run in 90 ml AnalaR quality $11M$ hydrochloric acid, a little at a time, allowing the reaction to subside after each addition (Note 1). After all the acid has been added, heat, if

TABLE I

*Solution**	*Aluminium added (µg)*	*Aluminium found*** (µg)
1	20	20.4
2	40	40.8
3	60	61.0
4	80	79.2
5	100	96.0

* All solutions contained 0.35 g beryllium per 20 ml.

** These recoveries have been corrected for the blank on the reagents and for the aluminium present as impurity in the beryllium.

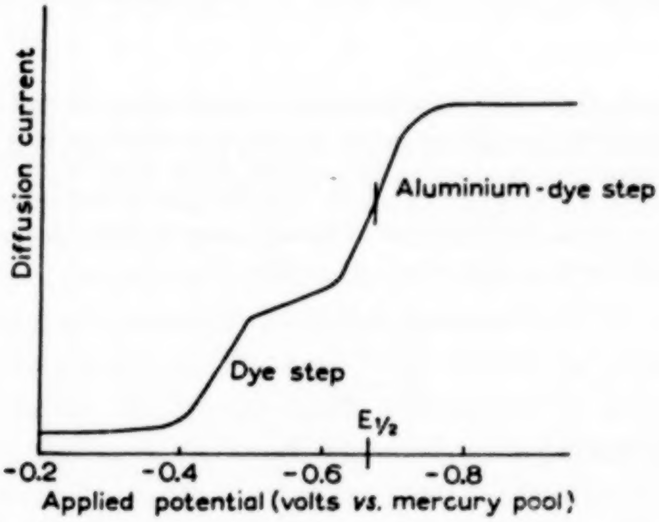

Fig. 2. Aluminium (40 µg) after separation by oxine extraction, removal of impurities by mercury-cathode electrolysis and addition of solochrome violet R.S. (sodium perchlorate–ammonium acetate base electrolyte). Final pH = 4.62.

necessary, to complete the dissolution. Wash down the beaker and cover with water, cool and transfer the contents to a 250-ml graduated flask. Rinse out the beaker twice with water and add the rinsings to the flask. Make up to volume with water.

Pipette 20 ml of the prepared solution (Note 2) into a 250-ml beaker and add 20 ml water. Add 40 ml of a solution of 8-hydroxyquinoline (oxine), prepared by dissolving 8 g of the oxine in 40 ml of glacial acetic acid and diluting to 1 l. Adjust the pH to 5.0 by addition of a solution of sodium acetate (375 g sodium acetate dissolved in 500 ml water) from a burette. (Note 3). Boil for 5 min, allow to cool to room temperature and transfer to a 250-ml separating funnel. Extract four times with 10-ml portions of redistilled chloroform. Finally, reject the aqueous layer. Transfer the combined chloroform extracts to a 250-ml separating funnel and extract with 10 ml of $5N$ nitric acid. Collect the chloroform layer in a conical flask as soon as separation occurs and run off the nitric acid layer into a 100-ml tall-form beaker. (Note 4). Wash out the separating funnel with small volumes of water and add these to the nitric acid solution in the beaker.

Return the chloroform layer to the separating funnel and repeat the extraction three times with 10-ml portions of $5N$ nitric acid. Combine all extracts and washings in the 100-ml beaker.

Add 1 ml of 20 vol% hydrogen peroxide and evaporate the solution almost to dryness in the presence of an "antibump" rod. Wash down the beaker periodically during the evaporation with $16M$ nitric acid.

Allow to cool, add 2 ml of $18M$ sulphuric acid and heat the solution until fuming strongly. Carefully add $16M$ nitric acid down the side of the beaker (Note 5). Repeat the addition of nitric acid, replacing when necessary, the sulphuric acid lost by fuming, until on evaporation to dryness the residue is white.

Wash down the beaker with 10 ml of water, add 5 ml of $5N$ perchloric acid and warm until the residue is completely dissolved. Transfer to a 25-ml graduated flask and make up to volume with water. Place the solution in the cell of the mercury cathode electrolysis apparatus and electrolyse for 1 h at a cell current of 1 A as already described under EXPERIMENTAL.

After completion of the electrolysis, pipette 20 ml of the solution into a 100-ml tall-form beaker and evaporate, in the presence of an "antibump" rod, until the residue is just moist. Wash down the beaker with 5 ml of water and warm until the residue dissolves, cool, add one drop of methyl red indicator, followed by 10% sodium hydroxide solution until just alkaline. Add 2.5*N* perchloric acid dropwise until the solution is just acid and then a further 1.0 ml in excess. Add 2.0 ml of 2.5*N* ammonium acetate solution followed by 10 ml of a 0.065% aqueous solution of solochrome violet R.S. Transfer to a 25-ml graduated flask and make up to volume with water. Immerse the flask for 5 min in a beaker of water heated to 60°–70°. Cool to room temperature and transfer an aliquot to a polarographic cell.

Deoxygenate for 5 min and record a polarogram at 25° over the range −0.45 to −1.1 V, using the mercury pool as anode. Measure the height D_1 of the step which occurs at about −0.67 V. Calculate the concentration of aluminium in the sample from the expression:

$$\text{p.p.m. Aluminium} = \frac{(D_1 - D_2) \times P_1 \times F_x \times 125}{32}$$

where D_2 is the aluminium step height obtained as described under *Blank determinations* and *F* is the factor obtained as described under *Calibration*. P_1 is the sensitivity setting of the polarograph.

Calibration

Dissolve 0.420 g AnalaR quality aluminium ammonium sulphate $AlNH_4(SO_4)_2 \cdot 12H_2O$ in 100 ml water containing 2.0 ml of 60% perchloric acid. Dilute the solution to 500 ml with water. Place 2.0 ml of the prepared solution into a 25-ml measuring flask and carry out the neutralisation to methyl red addition of perchloric acid, ammonium acetate and solochrome violet R.S. as described in the method. Then carry out the heating and polarography as also described. Measure the height, D_3, of the aluminium step which occurs at about −0.67 V.

Calculate the factor *F* from

$$F = \frac{100}{P_2 \times D_3}$$

where P_2 is the sensitivity setting of the polarograph.

Blank determinations

Place 3.0 ml of the 11*M* hydrochloric acid in a 250-ml beaker and carry out the determination as described in the method from the addition of oxine to the polarography. Measure the height, D_2, of the aluminium step occurring at about −0.67 V, making the appropriate correction for instrumental sensitivity.

Notes

1. Dissolution is very vigorous and it may be necessary to cool the beaker in an ice bath.
2. The procedure should be carried out in duplicate from this point.
3. A pH meter should be used for this adjustment.
4. The first extraction should be performed as quickly as possible (within 1 min) otherwise a yellow precipitate forms in the separating funnel.
5. Great care is necessary in this operation or material will be lost due to violent spitting.

TRIAL OF THE METHOD

A number of determinations of aluminium in samples of beryllium metal were made in order to obtain information regarding the accuracy and precision obtainable. The results obtained in the presence and absence of aluminium are given in Table II below.

DISCUSSION

LATIMER quotes standard electrode potentials for aluminium[6] and beryllium[7] as —1.906 and —2.096 V *versus* S.C.E. respectively. In the absence of complexing agents, therefore, the interference, of a large beryllium step with the aluminium step would make direct polarography impossible.

The half-wave potentials given in the literature for the interfering elements, are well below the potential at which aluminium mosses might be expected. In the case

TABLE II

Sample	*Aluminium added (p.p.m.)*	*Aluminium found (p.p.m.)*
A	0	399
A	50	447
B	0	78
B	50	125
B	100	179
C	0	110
C	50	164
D	0	58
D	50	110

of uranium, however, the deposition of this element will only occur at a potential more negative than that which can be employed without loss of aluminium, but the uranium will probably be reduced to the trivalent state. In the case of nickel, reduction is known to be irreversible except under special conditions[8] and KOLTHOFF AND LINGANE[9] quote —1.1 V for the half-wave potential in non-complexing media. The measured half-wave potential of —1.385 obtained in earlier work[10] indicated that the removal of this element is less easy than might be expected. The results show that, as expected, total deposition of the interfering elements without loss of aluminium is achieved without a very rigid control of applied voltage, although the difficulty of removing the last traces of iron is in accordance with the above considerations. The non-interference of uranium appears to indicate that in its lower valency state it does not react with solochrome violet R.S. under the conditions employed.

SUMMARY

A description is given of the application of the polarographic determination of aluminium using solochrome violet R.S. (discussed in Part I of this series) to the determination of microgram amounts of this element in beryllium metal. The method involves the removal of the aluminium from the bulk of the beryllium and from certain other elements by extraction with 8-hydroxyquinoline into chloroform. After destruction of the oxinate and removal of iron and other interfering elements still remaining, by mercury cathode electrolysis, the aluminium is determined polarographically. Results are presented and some theoretical aspects are discussed.

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A POLAROVOLTRIC METHOD FOR HALOGEN ION DETERMINATION IN DILUTE SOLUTION

by

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INTRODUCTION

The empirical bases of the polarovoltric titration method, details of an apparatus for simple end-point reading (commercial name "Titravit"), and some examples in its field of application have been described elsewhere[1,2,3]. Briefly, the Titravit records the difference between an adjustable reference voltage and the polarisation voltage set up between two platinum micro-electrodes in a solution. When the concentration of the ion or ions causing the polarisation is changed by titration of the solution, the polarisation voltage changes correspondingly. The equation $d = f(v)$, where $d =$ the total (cumulative) deflection of the Titravit microammeter and $v =$ the volume of added titrant, thus represents the titration curve of the solution in which the electrodes are dipped. It is well kown that near the equivalence point of a titration, large relative changes occur in the concentrations of the ions reacting in the titration. The curve $d = f(v)$ will, under favourable conditions, thus have an inflection, the steepest part of which can be taken as the end-point of the titration.

In precipitation titrations of halides with silver nitrate, the Titravit responds to the appearance of silver ions in the solution; the disappearance of halide ions is also recorded to some extent. The zone of maximum sensitivity of the titration curve $d = f(v)$ occurs at a silver ion concentration of about 10^{-4} to 10^{-7} mol/l, depending chiefly on electrode size, speed of stirring and temperature. It can be calculated that the equivalence point of the titration of a halide with silver nitrate occurs theoretically when $[Ag^+] = [Hal^-] = \sqrt{k}$, where $k =$ the solubility product of the silver halide. This gives about 10^{-5} mol/l for chloride, 10^{-6} for bromide and 10^{-8} for iodide. The end-point given by the Titravit could be made theoretically to correspond to these concentrations by regulation of electrode size and stirring speed, so that end-point and equivalence point would be identical. In practice, however, many factors like adsorption of ions on the precipitate or the effect of particle size on the solubility product value, interfere with theoretically derived values. In the present work, a higher end-point silver ion concentration has been ensured, with consequent slight overtitration. A correction procedure, described below, was then applied.

CORRECTION PROCEDURE

Two titrations are carried out:

(i) The usual titration with silver nitrate solution of an aliquot of halide solution to the accepted end-point.

(ii) The titrated solution from (i) is diluted with a measured volume of solvent and brought to the same end-point again by further titration with silver nitrate, or with the halide solution.

Assume that V ml of halide solution (say sodium chloride) of concentration C is titrated in (i) with v ml of silver nitrate, concentration c mol/l. The total volume of the solution is then $V + v$. To simplify calculations, let this volume be doubled, *i.e.*, $V + v$ ml solvent are now added, after which a further titration of δv ml silver nitrate is needed to attain the end-point again.

The following two equations hold for the ionic concentrations in solution:

$$[Ag^+]\,[Cl^-] = k \text{ (solubility product)} \quad \ldots\ldots\ldots\ldots \quad (1)$$

$$[Ag^+] + [Na^+] = [Cl^-] + [NO_3^-] \text{ (electric neutrality of the solution)} \quad \ldots \quad (2)$$

From (1) and (2), we obtain

$$[Ag^+] - k/[Ag^+] = [NO_3^-] - [Na^+] \quad \ldots\ldots\ldots\ldots \quad (3)$$

After titration (i), equation (3) becomes

$$[Ag^+] - k/[Ag^+] = cv/(V+v) - CV/(V+v) \quad \ldots\ldots\ldots \quad (4)$$

After titration (ii), it becomes if $\delta v \ll (v+V)$

$$[Ag^+] - k/[Ag^+] = c(v+\delta v)/2(V+v) - CV/2(V+v) \quad \ldots\ldots \quad (5)$$

Since the indicator system functions by demonstrating the presence of a definite $[Ag^+]$, this must be the same after each titration, so that the left hand sides of equations (4) and (5) are equal. Equating the right hand sides, we arrive at the relation:

$$C = c(v - \delta v)/V$$

If under-titration has occurred in (i), so that it is necessary in (ii) to titrate with halide solution (δV ml), the corrected concentration is given by:

$$C = cv/(V - \delta V)$$

A similar calculation is possible on the basis of dilution by a factor other than two, and also if the indicator system functions through the halogen ion concentration reaching a definite value.

Foreign electrolytes or compounds should be added if practicable so that they have as nearly as possible the same concentration at the end of (ii) as the end of (i).

This correction procedure appears to possess at least one marked advantage over the scheme in which a blank titration is made on a separately prepared, saturated solution of the silver halide. The reaction conditions (condition of the precipitate, speed of stirring in the neighbourhood of the electrodes, temperature) are more likely to be essentially the same in each titration when dilution by further solvent is carried out than when a fresh solution is prepared from solid precipitate. This latter preparation is also time-consuming and in addition, the light-sensitivity of the solid halide introduces an additional complication.

EXPERIMENTAL

Apparatus

All titrations were carried out in a 100-ml tall beaker with a small rounded depression in the centre of the base, placed on a magnetic stirring unit containing a corresponding depression in the centre of its surface. The polyvinylchloride-covered stirring magnet then rotated very smoothly and regularly even at fairly high speeds, with its rim in the depression. This smooth stirring, avoiding the customary sliding from side to side, is essential in obtaining the best and most reproducible results in polarovoltric titration.

The size of the magnet was 2 × 0.5 cm and the speed of rotation was about 500 r.p.m.

The commercially available Titravit apparatus was used.

The platinum electrodes were 2 cm × 0.3 mm, melted into a double glass capillary. For use in more concentrated halide solutions, the electrodes were more widely spaced in order to prevent formation of a short-circuiting bridge of precipitate between the electrodes.

Solutions

NaCl: 0.02 and 0.004N each by dilution of Merck "Titrisol" solutions.
KCl: 0.02 and 0.004N, each by weighing Prolabo KCl pour analyses (99.8%).
KBr: 0.02 and 0.004N, each by weighing Prolabo KBr pour analyses (guaranteed minimum of 99.5% KBr).
KI: 0.02 and 0.004N, each by weighing Merck KI pro analysi (highest quoted impurity of 0.1 %).
$AgNO_3$: approx. 0.1N, by weighing ordinary reagent grade salt.
$AgNO_3$: approx. 0.02N, by diluting the approx. 0.1N solution.
$Ba(NO_3)_2$: saturated aqueous solution.
Gelatine: 1% aqueous solution, saturated with potassium nitrate.

Titration procedure and results

Two experimental procedures were used:

1. Titrations of 0.02N halide with 0.1N silver nitrate solution. These were carried out in the presence of barium nitrate which served to accelerate flocculation and thus prevent its sudden onset near the end-point, which would disturb Titravit readings. 20 ml of halide solution and 10 drops of the saturated barium nitrate solution were used each time. The approximate shape of the titration curve $D = f(v)$ was determined by a preliminary titration. With its help, the

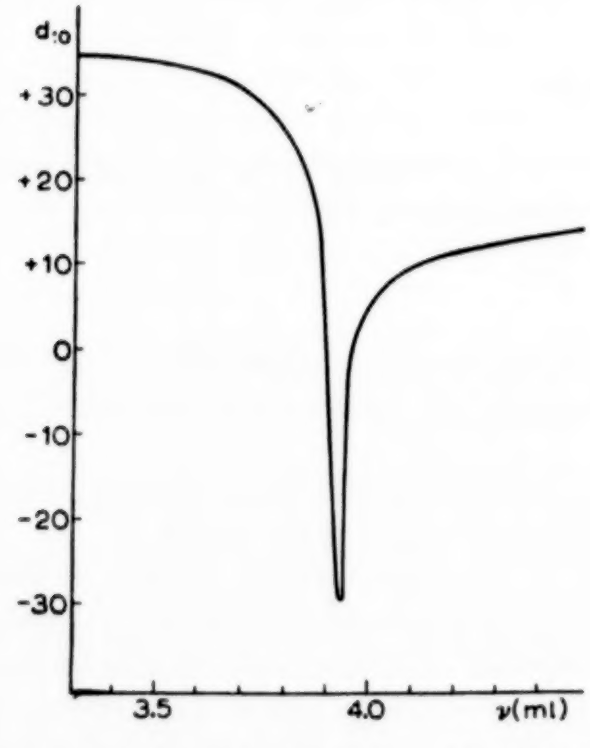

Fig. 1. Titration of 20 ml 0.01998N KI with $AgNO_3$, approx. 0.1N. v = volume of added $AgNO_3$; d = instrument deflection*.

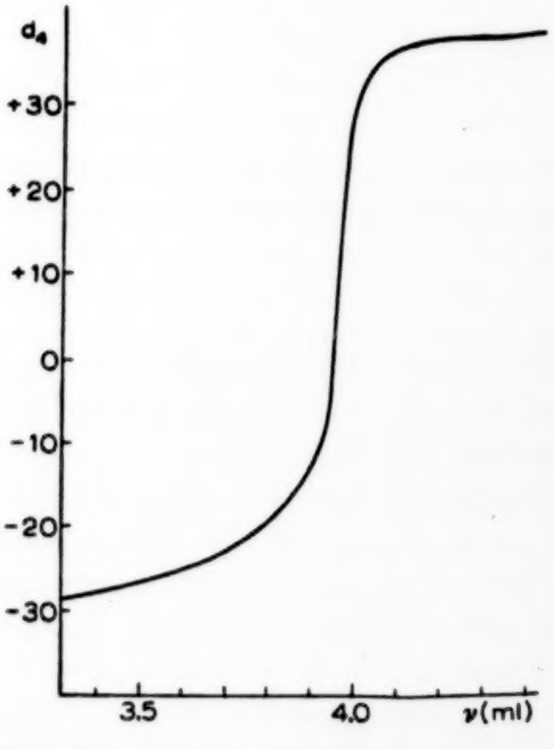

Fig. 2. Titration of 20 ml 0.02N NaCl with $AgNO_3$, approx. 0.1N. v = volume of added $AgNO_3$; d = instrument deflection*.

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* The subscript number expresses the sensitivity as the number of mV per scale division.

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reference voltage and sensitivity of the Titravit were regulated in order to ensure that the instrument pointer remained on the scale during the whole titration. Titrant was then added to an aliquot until one drop gave rise to a larger, permanent deflection, after which it was added drop by drop and the successive deflections read. When a further addition caused a smaller deflection than the preceding addition, the titration was complete. Plotting the titration curve was not usually necessary because the inflection point was recognisable by a much larger deflection.

Some results are given in Figs. 1 and 2 and in Table I.

TABLE I

Solution titrated	v' *(ml)*	f *Mean*	$\delta f/f$ *(%)*
20 ml KI	3.948	1.0122	0.02
$0.1998N$	3.947		0.01
	3.946		0.03
	3.949		0.04
	3.946		0.03
	3.950		0.07
	3.945		0.06
20 ml KBr	3.936	1.0143	0.02
$0.1970N$	3.937		0.00
	3.935		0.05
	3.940		0.08
20 ml NaCl	3.953	1.0124	0.06
$0.0200N$	3.950		0.01
	3.950		0.01
	3.948		0.06

v = volume of added silver nitrate; v' = titration to end-point; f = factor of the silver nitrate, calculated from the v'.

It is evident that the reproducibility of the results exceeds 0.1%. The results with potassium iodide and with sodium chloride agree very well, but the factor of the silver nitrate in the titrations of potassium bromide, deviates slightly. This deviation of about 0.2% may be related to the rather lower purity quoted for the bromide.

Comparison of Figs. 1 and 2 shows that the effective steepness of the titration curve at the end-point is markedly higher for iodide than for chloride.

The correction procedure was applied to some of the above titrations but gave negligible corrections in these more concentrated solutions.

It was found that the establishment of the voltage between the electrodes was appreciably faster and more reproducible in the presence of barium nitrate. This agrees with the claim that it produces similar effects in potentiometric titration[4].

2. *Titrations of $0.004N$ halide with $0.02N$ silver nitrate solution.* These were done in the presence of gelatine to eliminate errors caused by the electrodes becoming coated with flocculated precipitate, which were especially high in chloride titrations. 20 ml of halide solution + 10 drops of the gelatine solution were titrated. As above, a preliminary titration permitted regulation of the reference voltage and sensitivity of the Titravit.

The gelatine was saturated with potassium nitrate for two reasons: firstly, to add supporting electrolyte to the low halide concentration, since experience has shown

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that the Titravit functions better when the ionic concentration is not too low; secondly, because the whole work was primarily undertaken as the final stage in micro-halogen determination on organic compounds and the neutralised solutions from combustions usually contain potassium or sodium nitrate.

The solution was then titrated to a point on the inflection of the titration curve and the volume of added titrant and position of the instrument needle noted. The volume of solution was then doubled by addition of solvent + 10 drops of the gelatine solution, as mentioned above under "correction procedure". The instrument needle was then brought back to the noted position by further titration and the extra volume of titrant read.

Figs. 3 and 4 show two typical titration curve forms and some results are summarised in Table II.

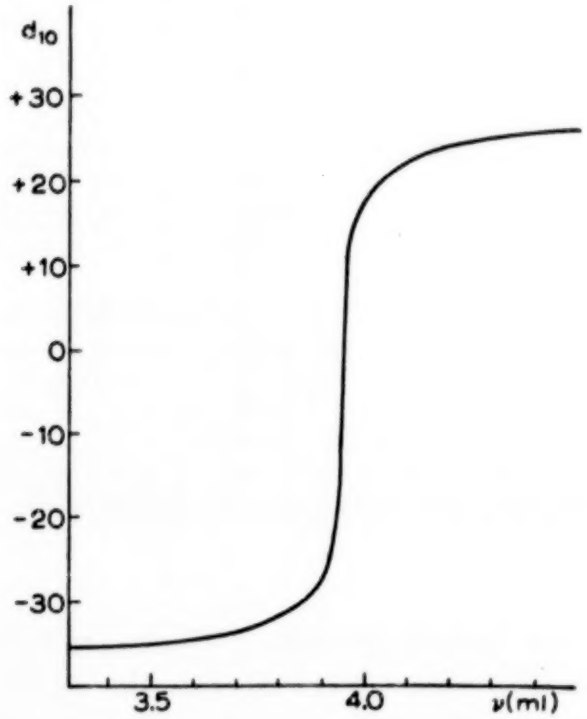

Fig. 3. Titration of 20 ml 0.00398*N* KBr with $AgNO_3$, approx. 0.02*N*.

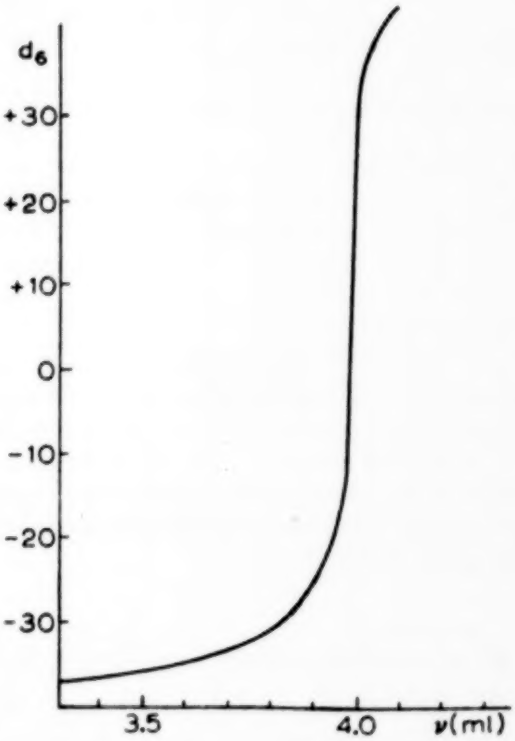

Fig. 4. Titration of 20 ml 0.00400*N* NaCl with $AgNO_3$, approx. 0.02*N*.

The titration curve still has a steep inflection, even in these dilute solutions. The reproducibility in general exceeds 0.2%.

The factor of the silver nitrate solution as determined by different halide titrations, is remarkably constant and essentially identical to that found for the 0.1*N* silver nitrate used above, from which the dilute reagent was prepared.

Comparison of Figs. 2 and 4 show that the gelatine evidently increased the steepness of the titration curve inflection to about 6–7 times that expected. It may thus be better to use gelatine of barium nitrate even in more concentrated solutions. KOLTHOFF AND KURODA[5] found that the use of gelatine yielded better results in the amperometric titration of halides with silver nitrate.

At the inflection, additions of about 0.007 ml of 0.02*N* silver nitrate to about 25 ml solution, a change in $[Ag^+]$ of about $5 \cdot 10^{-6}$ mol/l, caused a deflection of at least 10 scale divisions. Changes in $[Ag^+]$ of 10^{-6} mol/l can thus clearly be recorded and halide solutions of as low as 10^{-4} mol/l could be titrated with adequate accuracy.

References p. 637

TABLE II

Solution titrated	v' *(ml)*	$\delta v'$ *(ml)*	*Mean* $v' - \delta v'$	*Mean* f	$\delta f/f$ (%)
20 ml KI 0.00400N	3.969	0.031	3.943	1.014	0.12
	3.965	0.025			0.08
	3.970	0.024			0.08
	3.964	0.018			0.08
	3.961	0.016			0.05
(one month later)	3.984	0.026	3.961	1.010	0.08
	3.986	0.022			0.08
	3.985	0.024			0.00
20 ml KBr 0.00398N	3.960	0.030	3.926	1.014	0.10
	3.953	0.027			0.00
	3.952	0.029			0.08
20 ml NaCl 0.00400N	3.996	0.044	3.953	1.012	0.03
	3.992	0.045			0.15
	4.003	0.045			0.12
	3.994	0.046			0.13
	3.998	0.047			0.05
	4.005	0.046			0.15
20 ml KCl 0.00314N	3.140	0.047	3.101	1.013	0.25
	3.138	0.042			0.17
	3.140	0.033			0.20
	3.141	0.040			0.00
	3.142	0.038			0.10
	3.145	0.045			0.03
	3.156	0.050			0.17
10 ml KCl 0.00314N + 10 ml H_2O	1.597	0.047	1.552	1.012	0.13
	1.600	0.046			0.13

Notation as in TABLE 1; $\delta v'$ = second titration in correction procedure.

SUMMARY

The application of polarovoltric titration to halogen ion determination with silver nitrate solution has been described and the results quoted show that analysis of even highly dilute halide solutions is possible with an accuracy of about ± 0.2%.

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THE THERMOLYSIS OF SOME TRANSITION METAL CHELATES WITH 2-(*o*-HYDROXYPHENYL)-BENZOXAZOLE

by

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The use of 2-(*o*-hydroxyphenyl)-benzoxazole (HPB) for the gravimetric determination of cadmium was introduced by WALTER AND FREISER[1]. They found that the chelating agent was fairly selective for cadmium ions and that the metal chelate possessed excellent thermal properties. In fact, there was no color change when the chelate was heated up to 275° in a capillary tube and no sign of melting even at 300°.

Further use of this reagent was made by BYRN AND ROBERTSON[2] who found that copper(II) ions could be selectively precipitated in the presence of ethylenediaminetetraacetic acid as a masking agent. The copper chelate, in this case, was dried at 130–140°.

CHARLES AND FREISER[3] have shown that a number of other metal ions are also precipitated by HPB. The Cu(II), Ni, Zn and Co(II) HPB chelates showed no evidence of melting or decomposition at 300°, the highest temperature they tried. They found, however, that the lead HPB chelate began to decompose at about 280°, but did not melt at 300°.

In view of the excellent thermal stability of this class of chelates and the potential uses of this reagent for the determination of Cd and Cu(II), it was of interest to study the HPB chelates of Cd, Cu(II), Co(II) and Ni on the thermobalance.

EXPERIMENTAL

Reagents

2-(*o*-Hydroxyphenyl)-benzoxazole was obtained from Eastman Organic Chemicals, Rochester, N. Y.

All other chemicals were of reagent grade quality.

Thermobalance

The thermobalance used had been previously described[4]. A heating rate of 5.4°/min was used.

Preparation of metal chelates

The cadmium HPB chelate was prepared as previously described[1].

The copper HPB chelate was prepared as previously described[2].

The other metal HPB chelates were prepared as previously described[3].

All of the metal HPB chelates were air dried at room temperature (25–29°) for at least 24 h before thermal decomposition on the thermobalance.

DISCUSSION

The thermal decomposition curves are shown in Fig. 1 with the metal chelate stability temperatures and minimum oxide level temperatures given in Table I. In general, the metal chelates possessed excellent thermal properties. After a slight weight loss due to absorbed moisture, the metal chelates began to decompose in the 165 to 285° temperature range. These results reveal that the metal chelates can be dried at fairly high temperatures before decomposition takes place. The metal oxide level temperatures began in the 500 to 595° temperature range. However, it would not be advantageous to ignite the metal chelates to the oxides because they possess favorable gravimetric factors and excellent thermal stabilities.

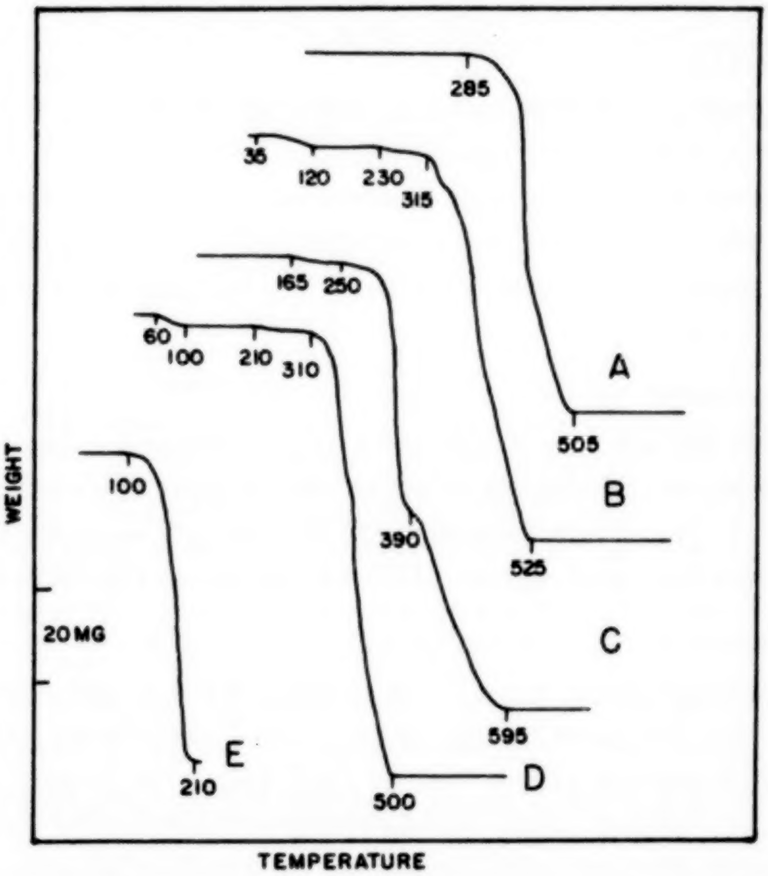

Fig. 1. The thermal decomposition of the metal HPB chelates.
A. Cadmium HPB chelate
B. Nickel HPB chelate
C. Copper(II) HPB chelate
D. Cobalt(II) HPB chelate
E. HPB

TABLE I

THERMAL PROPERTIES OF METAL 2-(*o*-HYDROXYPHENYL) BENZOXAZOLE CHELATES

Metal	*Chelate stability temp.* °*C*	*Minimum oxide level temp.* °*C*
HPB	< 100	–
Cadmium	< 285	> 505
Copper(II)	< 165	> 525
Cobalt(II)	< 210	> 500
Nickel	< 230	> 525

2-(o-Hydroxyphenyl)-benzoxazole

The reagent was first studied on the thermobalance to determine its thermal properties. If the reagent possessed a favorable sublimation temperature or boiling point, it may be possible to remove any coprecipitated reagent in the metal chelates by heating. However, this was not found to be the case.

The reagent began to lose weight at 100°. Beyond this temperature the weight loss was rapid, resulting in a small amount of carbonaceous matter in the thermobalance pan at 210°. The melting point of the compound was 124–126°, hence, there was some weight loss before it melted.

Cadmium HPB chelate

The air dried cadmium HPB chelate was stable up to 285°. Beyond this temperature, the chelate decomposed rapidly, giving the CdO level at 505°. From the thermal decomposition curve, the drying temperature of 130–140° previously suggested[1] appears justified. However, higher temperatures may be employed if necessary. The cadmium chelate was the most stable of all of the HPB metal chelates studied in this investigation.

Copper(II) HPB chelate

The copper HPB chelate was stable up to 165°. Beyond this temperature, a slight weight loss occurred, becoming more rapid above 250°, and finally giving the CuO level at 595°. Again, the drying temperature of 130–140° appears to be justified[2]. The Cu HPB chelate was the least stable of all of the metal chelates studied.

Nickel HPB chelate

The thermal decomposition curve of the nickel HPB chelate revealed that a small amount of water was retained by the chelate after air drying. This water began to come off at 35° and was completely lost at 120°. From 120 to 230° a horizontal weight level appeared which corresponded to the anhydrous chelate. At 230° the chelate began to lose weight slowly. Beyond 315°, however, the chelate decomposed rapidly, giving the NiO level at 525°.

Cobalt(II) HPB chelate

The thermal decomposition curve of the Co HPB chelate was almost identical to that of the Ni chelate. Absorbed water began to come off at 60° and was completely lost at 100°. The anhydrous chelate was stable between 100 and 210°. Beyond 210°, however, the chelate began to decompose slowly. Above 310° the decomposition became quite rapid to give the Co_3O_4 level beginning at 500°.

SUMMARY

The thermal decomposition of the 2-(o-hydroxyphenyl)-benzoxazole chelates of Cd, Cu(II), Co(II), and Ni were studied on the thermobalance. The metal chelates possessed excellent thermal properties. The first weight losses for the chelates appeared in the 165 to 285° temperature range. The minimum metal oxide levels appeared in the 500 to 595° temperature range.

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REVUES DE LIVRE

Chromatography, A review of principles and applications, par E. LEDERER ET M. LEDERER, second Edition, Elsevier Publishing Company, Amsterdam, 1957, 711 pages, Prix £ 3.12.–.

En 1953 Messieurs E. ET M. LEDERER faisaient paraître un remarquable traité de chromatographie de 396 pages et 1879 références bibliographiques qui a eu un très grand succès. Il n'est, pour se faire une idée de l'extraordinaire développement de cette méthode de séparation que de remarquer que la seconde édition de cet ouvrage qui vient de sortir de presse a 628 pages et 3704 références. C'est dire aussi qu'il a été profondément modifié et considérablement augmenté dans toutes ses parties en tenant compte des travaux publiés au cours de ces toutes dernières années.

Les principales divisions de ce traité sont:

1. La chromatographie par adsorption qui comprend, entre autres, les diverses techniques en usage, l'appareillage, les adsorbants et les éluants, la chromatographie des substances incolores, la chromatographie d'adsorption des gaz.
2. La chromatographie par échangeur d'ions dont les principaux chapitres sont: Les résines de synthèse, les équilibres et le comportement des composés organiques dans la colonne échangeurs d'ions.
3. La chromatographie de partage sur colonne et sur papier et la chromatographie gaz–liquide.
4. La chromatographie des substances organiques, vaste partie de 279 pages, dont les principales subdivisions sont: les hydrocarbures, les alcools et les phénols, les aldéhydes et cétones, les acides, les composés halogénés, les composés sulfurés, les hydrates de carbone, les lipides, les amino-acides, les peptides, les protéines, les purines, les pigments naturels, les vitamines, les hormones, les antibiotiques, la séparation des hauts polymères et enfin la séparation de stéréoisomères.
5. La chromatographie des substances inorganiques avec les adsorbants inorganiques et organiques, les séparations dans la colonne échangeur d'ions, la chromatographie inorganique sur papier et la séparation chromatographique des isotopes.

Cet ouvrage se termine par une liste extrêmement complète des références bibliographiques qui vont jusqu'en 1956. Un livre complet, fort bien présenté, dont l'exposé est net, intelligible. Si les auteurs n'ont pas développé de façon approfondie les bases théoriques de la chromatographie, ils ont su en prendre l'essentiel et les présenter avec clarté et concision et ce n'était pas chose facile. La partie technique et les applications sont exposées avec goût et précision. 139 figures et photographies très soignées illustrent le texte de cet ouvrage remarquable en toutes ses parties.

D. MONNIER (Genève)

The development of titrimetric analysis till 1806, par E. RANCKE MADSEN, G. E. C. Gad, Publishers, Copenhagen, 1958, 239 p.

Trop souvent encore, on pense que l'analyse titrimétrique commence avec GAY-LUSSAC, ou bien, chez les personnes un peu mieux informées, avec DESCROIZILLES. L'auteur de ce livre nous montre d'une façon convaincante et en même temps extrêmement captivante que cette technique n'est point ,,tombée du ciel'' au début du 19ème siècle, mais qu'elle a connu une évolution bien assignable pendant le 18ème et même pendant le 17ème siècles.

En effet, l'auteur cite pour commencer, les travaux de ROBERT BOYLE qui décrivit déjà un indicateur acidimétrique, extrait d'un bois mexicain. En 1699, HOMBERG publia ses travaux remarquables sur la neutralisation des acides par la potasse et décrivit une espèce de matras ressemblant à nos ballons jaugés. GEOFFROY LE CADET s'occupa en 1729 également de recherches titrimétriques pour le contrôle des vinaigres. Ils suivirent les travaux de l'écossais FRANCIS HOME (1756) sur le blanchissage, de l'anglais LEWIS (1767) sur l'analyse des potasses à l'aide d'acide chlorhydrique, de l'allemand WENZEL (1777) se rapportant à la stoechiométrie, du suédois BERGMAN sur l'analyse des eaux minérales, de GUYTON DE MORVAUX, de KIRWAN et d'autres que nous passons sous silence, pour terminer avec les travaux si importants de DECROIZILLES qui effectua de véritables analyses titrimétriques. Un nombre de figures nous montre l'évolution de l'appareillage au cours du 18ème siècle. La documentation est très grande; l'auteur, dans sa bibliographie, cite 337 mémoires. La lecture de cet ouvrage est pourtant très agréable. Peut-être pourrait-on regretter que l'auteur donne une série de définitions qui ne soient pas universellement reconnues. Bien qu'il en donne un résumé à la fin du livre, et en admettant que du point de vue étymologique elles soient tout à fait acceptables, il nous semble qu'un essai historique ne soit pas propre à introduire des idées nouvelles dans le domaine de la terminologie.

Mais enfin cela n'a pas trop d'importance et ne diminue pas la valeur du livre dont la lecture est chaleureusement recommandée à tous ceux qui s'intéressent à l'histoire de la chimie.

C. J. VAN NIEUWENBURG (Delft)

ANNOUNCEMENT

SECOND CONFERENCE ON ANALYTICAL CHEMISTRY IN NUCLEAR REACTOR TECHNOLOGY

Gatlinburg, Tennessee (U.S.A.)
September 29, 30 and October 1, 1958

The Oak Ridge National Laboratory has announced that the Second Conference in a series of unclassified meeting on the role of Analytical Chemistry in Nuclear Reactor Technology will be held in the Civic Auditorium at Gatlinburg, Tennessee, on September 29, 30 and October 1, 1958. This meeting is a continuation of the first conference which was also held at Gatlinburg in November 1957. A brief news account of the discussions wich took place at that meeting was reported in the December 1957 issue of *Analytical Chemistry.*

At the first conference the subject matter of the papers dealt specifically with a review of recent developments in the analytical chemistry of important reactor materials. At the forthcoming conference, it is intended to continue these discussions but only with respect to those facets of analytical chemistry which relate specifically to analyses which are required prior to the start-up of nuclear reactors and similarly to the same functions as may be applicable during reactor operations. Analytical chemistry as is pertains to post-operational activities is believed to be a matter of sufficiently broad interest and scope to warrant the holding of separate, future, conferences on this aspect alone.

Two 3-hour sessions of technical presentations will be held each day during the three-day conference. The last hour of each session, except that on Tuesday morning, will be devoted to panel discussions of the respective subject matter of those sessions. The panel discussion on Tuesday will be held during the last hour of the afternoon session and will be concerned with the subject matter of the entire day.

It is intended that the program will be contributory and any worker in the field who feels that he has some worthwhile contribution to offer is encouraged and invited to participate in the program. Papers of any length which may require up to 30 min for presentation will be considered.

Abstracts of approximately 200 words should be submitted by July 1. Publication of the proceedings is anticipated and copies of all manuscripts received prior to October 1 will be included in the publication.

The tentative schedule of events is as follows:

MONDAY, SEPTEMBER 29

	Registration
Morning session	Particle-size analyses of reactor fuels intended for use in slurry-type reactors
Afternoon	Open